Journal
of
The Franklin Institute
Devoted to Science and the Mechanic Arts

Vol. 203 FEBRUARY, 1927 No. 2

PHENOMENON OF DIRECT-CURRENT SELF-EXCITATION IN VACUUM TUBES CIRCUITS AND ITS APPLICATIONS.*

BY

NICHOLAS MINORSKY, E.E.

Moore School of Electrical Engineering, University of Pennsylvania.

THE three-electrode vacuum tube steadily gains ground in various branches of electrical engineering. After its spectacular advent in the art of radio communication, numerous attempts have been made and are being made to apply its remarkable properties to uses other than radio. Most of the scientific and engineering progress was accomplished along the line of A.-C. applications of the three-electrode tubes. Very little progress was made in the use of tubes in direct-current circuits. Theoretically, the applications of vacuum tubes in this connection are very attractive; in fact, the tube constitutes a very sensitive relay without any inertia with very high ohmic resistance, which makes it especially well adapted to operate in series with highly inductive circuits (like the exciting circuits), since the time constant of the circuit is reduced and the control is much more rapid. However, the difficulties inherent to the existing schemes of D.-C. amplification handicap further progress in this direction considerably.

The present research was undertaken with the idea of eliminating a part of these difficulties, particularly the necessity of using very large grid batteries especially difficult to adjust when

* Communicated by the Author.

(Note.—The Franklin Institute is not responsible for the statements and opinions advanced by contributors to the JOURNAL.)

COPYRIGHT, 1927, by THE FRANKLIN INSTITUTE.

several stages of amplification are used. Incidentally, it was discovered that under certain conditions the vacuum tube system acquires entirely new properties if compared with those of an ordinary amplifier; namely, the performance of the vacuum tube under certain conditions is abrupt, similar to the action of an ordinary contact, reminding one of the characteristic of the so-called magnetron † at its critical point; this particular performance lends itself to important applications.

We propose first to review briefly the properties of the new scheme as a straight D.-C. amplifier, then as a regenerative D.-C. amplifier. This will permit us to acquire a better physical understanding of the new phenomenon of self-excitation of the vacuum tube in direct-current circuits which forms the primary object of this paper, and which is described in subsequent sections.

1. NEW TYPE OF DIRECT-CURRENT AMPLIFIER.

As previously stated, the main difficulty with multistage direct-current amplifiers consists of the necessity of having many grid biasing batteries. To avoid this, a scheme shown on Fig. 1 was employed. *A* and *B* are voltage amplification tubes. In the test made these were Western Electric 102*D* tubes. *C* is a power tube (W. E. 101*D* tube).

A steady potential difference of about 350 volts between the points *MN* is maintained by means of a small D.-C. generator *D*. *MN* represents a certain resistor which, in our test, was made of 25-watt lamps connected in series. The tube *A* works under a plate voltage corresponding to the voltage drop between the points *a* and *b* on the potentiometer; the tube *B* under the voltage between the points *c* and *d*, and the power tube *C* under the voltage between *e* and *f*. The tubes *A* and *B* have in series with the plate resistors R_1 and R_2, each about 200,000 ohms. The potential difference between *c* and *d* was staggered with respect to that between *a* and *b*, so that for a given grid voltage of the first tube *A* the potential of the controlling point *m* of this first tube will be about 1½ volts below the potential of the filament (point *c*) of the second tube, which corresponds approximately to the middle point of the rectilinear part of its characteristic. The same method is applied to give to the grid of the power tube *C* suitable potential with respect to its filament. The staggering of potentials (*ab*, *cd*, *ef*) eliminates the necessity of having

† See article by A. W. Hull, *A.I.E.E. Journal*, 1921.

the bias batteries between the points m, n and the grids of the tubes B and C, respectively. It is apparent that the filaments of the tubes A, B, C are at different potentials corresponding to the points a, c, e of the potentiometer to which they are connected, so, for that reason, it is impossible to use a common A battery; the filaments are heated for that reason by three independent secondaries of a small transformer whose primary is designed for 110 volts, 60 cycles. Assume first that the current flowing through the resistor between MN is large as compared with the average plate current fluctuations of the tube C when the amplifier works (the plate current of tubes A and B is at all times negligible, being of the order of magnitude of 1 milliampere or less). In this case, the system works as a straight D.-C. amplifier, since the magnitude of the voltages as well as the amount of their relative staggering does not change appreciably when the output of the power tube C varies. In the case under consideration, this condition arises when the current through the potentiometer is of the order of magnitude of one ampere, the variations in output of the tube C being only about 25–30 milliamperes. The potentials of the points a, b, c, etc., being once adjusted, do not need any further adjustment, and the system works as a very stable and reliable amplifier whose amplification can be readily calculated as that of an ordinary resistance coupled amplifier. In case the small generator D is driven by a motor from the power supply, it is advisable to put a ballast lamp in series with D (for instance, between N and D or M and D) to keep the current through the potentiometer constant. This type of performance is the simplest but is not very economical, since the resistor MN absorbs considerable power. Phenomena are much more interesting when the output current of the tube C becomes comparable with the normal current through the potentiometer; the performance of the system acquires in this case additional features.

2. REGENERATIVE PERFORMANCE OF THE ABOVE SCHEME.

Assume now that by inserting a greater resistance between M and N we reduce the current through the potentiometer, but still have the same voltage between M and N. The grid regulation of tube C changes the conductance of this tube considered as a parallel circuit between e and f which causes a redistribution

of currents and voltages in the whole system. Important reactions result from this redistribution.

We shall analyze the performance with respect to the scheme of three stages shown on Fig. 1. This number of stages is not essential; it was chosen only because the second stage in this case works in somewhat peculiar conditions, which were deemed of interest to be mentioned. These conditions exist also in case the number of stages is greater than three, but are not so apparent when the number of stages is two.

We shall specify certain practical simplifications which will enable us to proceed more easily with the analysis of the phenomena. Firstly, we shall neglect the effect of variation in the

FIG. 1.

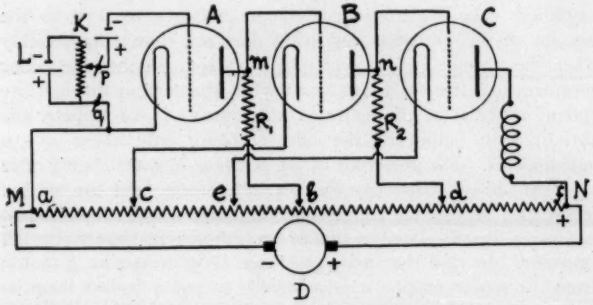


plate current of the tubes A and B upon the distribution of voltages and currents across the potentiometer and the power tube. In fact, in our case, these variations were of the order of magnitude of 0.5 milliampere or less, whereas the potentiometer current was 100 milliamperes, and the fluctuation of the output of the power tube C (in reality we had two 101D tubes in parallel) was about 50 milliamperes. Thus the whole redistribution of currents and voltages is due only to the variable conductance of the tube C.

Secondly, we shall neglect in the first study the effect of variation in the magnitude of the voltages between a, b, and c, d, respectively.

Assume that the potential of the grid of the tube A is increased by a small amount ε by means of a small D.-C. input

voltage between p and q, which may be derived from one dry-cell L through a potentiometer K. The space current in A increases, and the potential of the point m decreases, which lowers the grid potential of B, assuming that initially, the filament of B is at a fixed potential corresponding to the point c of the potentiometer. The decreasing space current in B causes an increase of potential at point n and increases the plate current of the power tube C. This is apparently equivalent to the increase of conductance between e and f through the tube C; therefore, the conductance of the part of the circuit between e and f is increased. The current delivered by the generator D is thus increased, which causes an increase in the potential difference between a and e and, therefore, a decrease of the potential difference between e and f since the terminal voltage between M and N is constant.

Since point a is chosen as the origin of potentials (in view of its connection to the filament of the first stage), the potential of point c rises in proportion to the total increase of the potential at e in which the resistance of ac is to the resistance of ae. Thus the space current in tube B is reduced not only because of the lowering of the grid potential (action coming from A), but also because of raising the filament potential (reaction coming from C), due to the change in the current and voltage distribution in the potentiometer. This constitutes the peculiar performance of the middle tube to which we referred in the beginning of this section. An analogous effect, but only in the opposite direction, occurs in the power tube; namely, the potential of the filament increases since the potential of point e goes up. The gain in amplification in the second tube, however, outweighs its loss in the power tube, due to a higher amplification of the second stage.

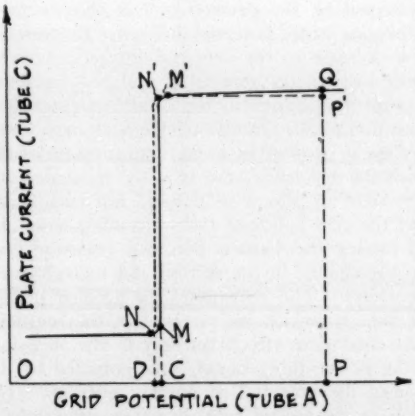
The amplifier in this case has a certain feed-back performance due to the redistribution of currents and voltages in the potentiometer. The amplification rapidly increases, but the performance becomes less stable.

3. PHENOMENON OF SELF-EXCITATION (CONTACT EFFECT).

If the amount of feed-back is still further increased, there is a real discontinuity in the performance which is illustrated by Fig. 2, representing the output current I_p of the power tube C plotted against the grid voltage of the first stage variable by means of a potentiometer K (Fig. 1). At a certain value OC of the grid potential, the plate current I_p of the last stage jumps

up abruptly from the value CM to CM'. It must be noted that the grid potential of the first stage does not change during this jump, since the potential of this grid is impressed from outside source. If, however, we reduce this potential by a slight amount CD, there occurs an abrupt change in the opposite direction (from N' to N). A slight increase of the grid potential from D to C will bring about a new jump from M to M', and so on. Any considerable increase in the grid potential (from C to P) generally causes only a slight change (QP') in the plate current;

FIG. 2.



the same applies also to the decrease of grid potential below D. The potential difference DC on the grid of the first stage is variable, depending upon the curvature of characteristics, as this will be explained later on. For the vacuum tubes in our test, it varies from about 5 to 20–30 millivolts (in one particular case it was reduced to $\frac{1}{10}$ millivolt), the jump in the plate current of the last stage (two 101D tubes in parallel) being always the same (about 35–40 milliamperes).

If the grid potential is fixed somewhere between D and C, the phenomenon is erratic. Sometimes the plate current jumps up to the high value (M'); sometimes it drops to the low value (M).

In summing up: There is no grid control in the narrow range

DC; outside this range the control exists corresponding to the ordinary performance of the system as an amplifier. The most interesting feature of the control occurs at the very edges of the narrow range *DC* where the slightest variation of the grid potential (to the right of *D* or to the left from *C*) acts as a trigger, releasing the phenomenon in one or the other direction.

The position of the zone *DC* can be shifted to different places of the grid potential range (for instance, by staggering the potentials of the filaments, by changing the amount of the plate resistors (R_1R_2, etc.)), but for a given combination of parameters, it stays put with a remarkable degree of precision; the discontinuity occurs always at a strictly identical point of the grid voltage of the first tube.

Originally the reason for this discontinuity was sought in the possibility of a spontaneous A.-C. self-excitation, but this idea was soon abandoned, since not the slightest trace of A.-C. was discovered within the whole range of frequencies, beginning from the lowest audio up to the highest radio frequencies which might be reasonably expected. It was thus evident that the solution of the problem had to be sought in the peculiar circumstances of the direct-current performance.

4. CRITERION OF STABILITY OF AN ELECTRIC CIRCUIT.

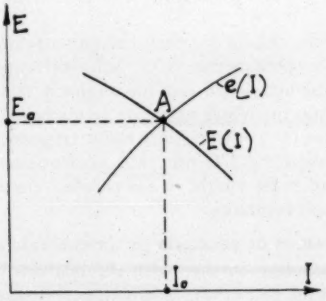
Before proceeding further with the analysis of this phenomenon, it is useful to review briefly the so-called "criterion of stability" formulated in a very general form by Kaufmann.‡

We propose to investigate the equilibrium condition in a system formed by two or several electric circuits interconnected in a certain manner. As an example, this system can be a shunt D.-C. generator, one circuit being the armature, the other its field, and the third the external circuit. All three circuits are in parallel across the brushes. Series or compound generators, an electric arc fed through a fixed resistance and many other known circuits may be considered as other examples. The same general questions arise: Which condition of the given circuit is stable and which is unstable, and what are the factors determining the stability or the instability of the system in general? We shall consider the simplest case of two circuits. This will be the case,

‡ W. Kaufmann, *Ann. d. Phys.* (4), **2**, 158, 1900. A. Blondel pointed out that a similar criterion was used by him in his investigations nine years prior to Kaufmann's publication.

for instance, of a shunt generator at no-load. To discriminate between the two circuits, we can call one the *generating circuit* (or simply the generator) and the other the *receiving circuit* (or simply the receiver), the differentiation being made on the consideration of the exchange of energy between the circuits. Thus, in the above example, the armature circuit is the generator, and the field the receiver circuit, respectively. In many cases, this distinction is less marked, and one has to use one's judgment in the choice of which part of the circuit can be considered as the generator and which as the receiver. Let $E = E(I)$ represent a

FIG. 3.



certain functional relation between the voltage across the generator terminals in function of the current I flowing through the generator circuit and let $e = e(I)$ be a similar relation for the receiver circuit. Representing $E(I)$ and $e(I)$ graphically (Fig. 3), the point A of intersection gives a possible condition of equilibrium

$$E(I) = e(I), \tag{1}$$

although at this stage of our consideration we do not know whether the equilibrium is stable or unstable at this point.

We shall define the equilibrium as stable when a small departure of the system from this equilibrium position disappears spontaneously in the course of time if the system is abandoned to itself.

Let E_0, e_0, I_0 be the values of E, e, I corresponding to the equilibrium condition, and E_1, e_1, I_1 small increments which occur

in these values when the system departs slightly from its original condition. Then $I = I_0 + I_1$; $E = E_0 + E_1$ and $e = e_0 + e_1$. Since for this new point there is no more equilibrium, the generator voltage is not equal to the receiver voltage statically, but instead of it there exists the well-known dynamical relation:

$$E = e + L\frac{dI}{dt} \text{ otherwise: } E_0 + E_1 = e_0 + e_1 + L\frac{d(I_0 + I_1)}{dt} \tag{2}$$

and since $E_0 = e_0$ and $\frac{dI_0}{dt} = 0$ (I_0 being a constant current corresponding to equilibrium), one has

$$E_1 = e_1 + L\frac{dI_1}{dt}. \tag{3}$$

On the other hand, for the new point, one has

$$E_0 + E_1 = E(I_0 + I_1). \tag{4}$$

The equation (4) expresses the fact that the new point $(E_0 + E_1)$ of the generator voltage corresponds to the new point $(I_0 + I_1)$ of the current through the same functional relation as before. Since I_1 is small, we can expand (4) in Taylor's series, and neglect all the terms beginning from the second order in I_1; this gives:

$$E_0 + E_1 = E(I_0) + I_1\left(\frac{\partial E}{\partial I}\right)_{I = I_0}. \tag{5}$$

Since $E_0 = E(I_0)$ one has:

$$E_1 = I_1 \cdot E'(I_0) \tag{6}$$

where $E'(I_0)$ denotes $\left(\frac{dE}{dI}\right)_{I = I_0}$; in a similar manner

$$e_1 = I_1 e'(I_0) \tag{7}$$

where

$$e'(I_0) = \left(\frac{de}{dI}\right)_{I = I_0}.$$

Eliminating E and e from the equations (3), (6) and (7), one has

$$I_1(e' - E') + L\frac{dI_1}{dt} = 0,$$

transposing

$$\frac{dI_1}{dt} = -\frac{1}{L}(e' - E')I_1. \tag{8}$$

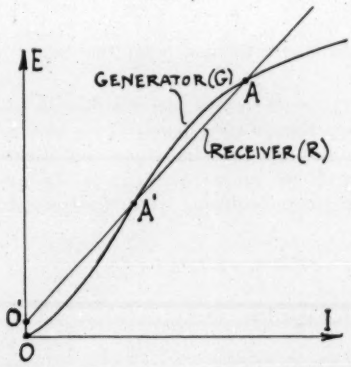
Similar equations can be drawn for E_1 and e_1.

The equation (8) shows that for a given disturbance I_1 the equilibrium is stable (that is, $\frac{dI_1}{dt} < 0$, which means that the disturbance decreases with the time) when

$$e'(I_0) - E'(I_0) > 0. \qquad (9)$$

The condition (9) constitutes the Kaufmann criterion for stability; it can easily be thrown into a simpler geometrical form, noting that geometrically $e'(I_0)$ and $E'(I_0)$ are the slopes of the

FIG. 4.



respective tangents to the curves $e = e(I)$ for the receiver, and $E = E(I)$ for the generator at the point of equilibrium I_0.

Kaufmann's criterion of stability can therefore be formulated as follows:

(1) *The equilibrium of an electric system is stable when the slope of the tangent to the characteristic of the receiver ($e = e(I)$) at the point of equilibrium is greater than the corresponding slope for the generator.*

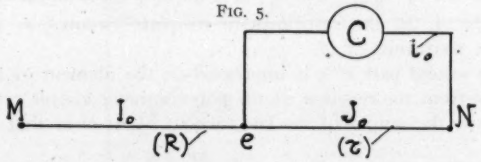
(2) *The equilibrium is unstable in the opposite case* ($E'(I_0) - e'(I_0) > 0$). For example, the equilibrium is stable at point A in the case of the self-excited shunt generator (Fig. 4) and unstable at A', OO' representing the induced voltage due to the residual magnetism.

5. STABILITY OF THE CIRCUIT SHOWN ON FIG 1.

The application of Kaufmann's criterion will enable us to explain the cause of the above-described discontinuity in the performance of the scheme shown in Fig. 1.

The distribution of currents and voltages in the system is due to changes in the output of the last (power) tube *C;* these changes depend on the grid potential of this last tube which in its turn depends upon the changes in the output of tube *C*. We see thus that it is impossible to state which is the effect and which is the cause, since the two effects are physically interlocked, forming parts of the same phenomenon; exactly similar conditions arise in the case of self-excitation of an ordinary D.-C. shunt generator. We can conventionally assign the rôle of the generator to the static (plate current-grid voltage) curve of the last tube and that of the receiver to the grid voltage considered as a function of the plate current. This last function is to be deter-

FIG. 5.



mined now. Referring to Fig. 5 (representing Fig. 1 in which tubes *A* and *B* are omitted since the variation in their output has no appreciable effect on the potential distribution along the potentiometer), I_0, J_0 and i_0 represent the initial values of currents between *Me*, *eN* and in the *C* tube, respectively. When the plate current changes by the amount i, I_0 and J_0 undergo respective changes: I and J. The application of Kirchoff's laws to the circuit before and after this change gives

$$I_0 = i_0 + J_0 \text{ and } I_0R + J_0r = E_0$$

before the regulation, and

$$I_0 + I = (i_0 + i) + (J_0 + J) \text{ and } (I_0 + I)R + (J_0 + J)r = E_0$$

after the regulation. Therefore

$$I = i + J \text{ and } IR = -Jr. \qquad (10)$$

Elimination of I between the two equations (10) gives

$$J = -\frac{R}{R+r}i,$$

and the substitution of J into the first equation (10) gives

$$I = \frac{r}{R+r} i,$$

wherefrom

$$e = IR = \frac{Rr}{R+r} i. \tag{11}$$

Equation (11) gives the potential variation e of the point e on the potentiometer (Fig. 1) in function of variation i of the plate current of the C tube. The variation e_1 of the filament potential of the second tube B (see Fig. 1) is proportional to e, namely:

$$e_1 = Ke = K \frac{Rr}{R+r} i, \text{ where } K = \frac{\text{resistance between } ac}{\text{resistance between } ae}. \tag{11'}$$

The voltage V_2 controlling the second tube B is composed of two parts: The first part V'_2 is impressed on its grid and arises from the regulation of the first stage A. This part is easily calculated; its value is $V'_2 = \frac{\mu_1 R_1 \varepsilon}{R_1 + \rho_1}$, where μ_1 is the amplification factor of the first tube A, R_1 the resistance in its plate circuit,§ ρ_1 plate to filament resistance of A.

The second part V''_2 is impressed on the filament of tube B; it arises from the reaction of the potentiometer circuit caused by changes in the output of the last tube C. It is clear that

$$V''_2 = e_1 = K \frac{Rr}{R+r} i.$$

Since the variations of potentials of the grid and the filament in the second tube B are always in opposite directions

$$V_2 = V'_2 + V''_2 = \frac{\mu_1 R_1}{R_1 + \rho_1} \varepsilon + K \frac{Rr}{R+r} i.$$

We shall limit our investigation to the case when the potential of the grid of the first stage acquires a certain fixed small change ε; then $V_2 = a + bi$, where $a = \frac{\mu_1 R_1}{R_1 + \rho_1} \varepsilon$ and $b = K \frac{Rr}{R+r}$ are two constants. Thus the voltage V_2 controlling the second stage is a linear function of i. Two distinct cases are possible:

(1) The second stage works substantially on the rectilinear part of its characteristic during the whole range of discontinuity occurring in the last tube.

(2) The second stage leaves the rectilinear part of its charac-

§ For reference see R. W. King, "Thermionic Vacuum Tubes." In our case the resistance R_1 can be used instead of impedance Z.

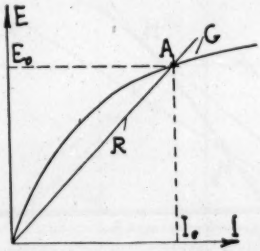
teristic in the first case to a linear variation ($V_2 = a + bi$) of its control voltage. This corresponds also to a linear variation of its plate current and a linear variation of the potential V_3 of point n controlling the grid of the power tube. Therefore V'_3 can be represented as $V'_3 = A' - B'i$, where A', B' are certain constants differing from a, b by the constant factors resulting from the parameters of the second stage; the minus sign is due to the fact that V'_3 decreases when V_2 increases, and *vice versa*.

The potential V_3 controlling the power tube is also composed of two parts, V''_3 arising from the grid control, and V'''_3 from the filament control:

$$V_3 = V'_3 + V''_3 = A - B'i - \gamma i,$$

where γ is given by equation (11). The control voltage $V_3 = A -$

FIG. 6.



Bi ($B = B' + \gamma$) is thus a linear function of i. The minus sign simply means that we have taken as the starting-point the second stage B. If we take the first stage, this sign must be reversed, since with the usual method of coupling (the coupling resistors are in the plate circuit) each subsequent tube reverses its variations. Finally

$$V_3 = A + Bi \qquad (12)$$

if we consider the whole phenomenon from the grid of the first stage.

The performance of the whole circuit is thus reduced to the study of the last stage.

The "generator" curve G of this stage (see Fig. 6) is its static curve (or dynamic if external impedance is inserted in its plate circuit).

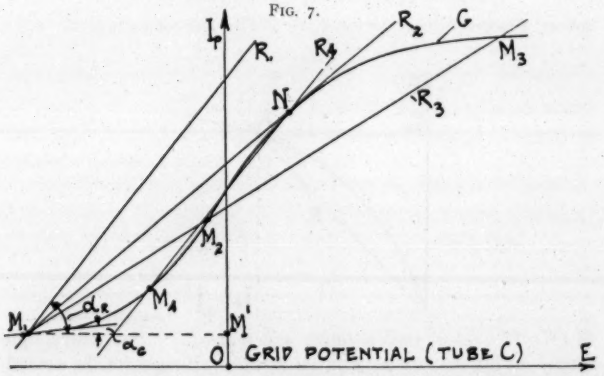
The receiver curve R (which is the straight line here) is

given by equation (12). Fig. 6 represents G and R curves for an ordinary D.-C. self-excited shunt generator in order to emphasize the physical analogy between the two cases. Fig. 7 illustrates the performance of the scheme in question.

If the line R occupies the position R_1 the plate current OM'_1 is low, and does not change much by the grid control of the first stage. The performance at point M_1 is stable, since, according to the criterion of Kaufmann, the slope α_R of the tangent to the receiver characteristic is greater than the corresponding α_G slope to the generator characteristic.

If, by changing the parameters A and B of the line R, we

FIG. 7.



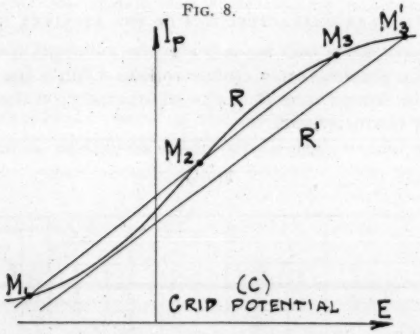
bring it into a position R_2 of tangency to G at N, we reach a critical case; point N is an equilibrium point but the application of Kaufmann's criterion shows that it is not a position of stable equilibrium $\alpha_R = \alpha_G$; strictly speaking, it is not a point of unstable equilibrium either—in fact, it is a point of indifferent equilibrium separating the zone of stability from that of instability. The slightest external impulse, however, will cause the systems to leave point N and to seek the only point of stability M_1.

If, by a still further change of parameters, the "receiver" characteristic R will come to R_3, there are three possible equilibrium positions: M_1, M_2, M_3, of which M_1 and M_3 are stable, and M_2 is unstable.

If the receiver characteristic R is shifted from R_1 to R_4

parallel to itself (which means analytically that B is kept constant, and only A varied), the phenomenon can be made very sharp; point M_4 is still a point of stable equilibrium, but is very near to a critical condition ($\alpha_R = \alpha_G$). The same remark applies to point N. A slight impulse tending to deviate the system from M_4 upwards or from N downwards will meet with insufficient inherent stabilizing tendency of the system to counteract this impulse and the operating point of the last tube will travel over the whole range from M_4 to N or *vice versa*, according to the direction of the incoming impulse; the latter, as we have seen, comes from the grid regulation of the first tube A which, for that

FIG. 8.



reason, cannot be considered, strictly speaking, as the first stage in the sense in which this expression is usually employed in connection with the thermionic amplifiers. In the present case, the first tube has the duty of a trigger only, enabling the system to exchange the two possible equilibrium positions, but the electric system subject to these changes of equilibrium is composed essentially of the tubes B and C.

The voltage V'_2 impressed on the grid of the second stage, and resulting from the changes in the input voltage of tube A enters as a component part in the developed expression of the parameters A and B of the receiver line R. To fix the ideas, assume that for given values of A and B the receiver line R occupies the position R as shown in Fig. 8, and the system remains at M_1 which is a point of stable equilibrium. Since the equilibrium is stable at this point, there is no reason why the

system should leave it if everything remains fixed. But, assume that by a slight change in the grid voltage of the first tube A the parameters of the characteristic line R have been changed in such a manner as to bring it from R to R'. The only point of stable equilibrium, as is apparent from the figure, is now M'_3. The system will swing from point M_1 corresponding to R, to M'_3 corresponding to R'. An inverse operation will cause the reversal of the phenomenon. The trigger voltage (D.-C. on Fig. 2) will be smaller the nearer the slope of the "receiver line" R will be to the slope of the rectilinear part of the "G curve," which in this case is the static characteristic of the tube.

6. CURVILINEAR CHARACTERISTICS OF THE RECEIVER CIRCUIT.

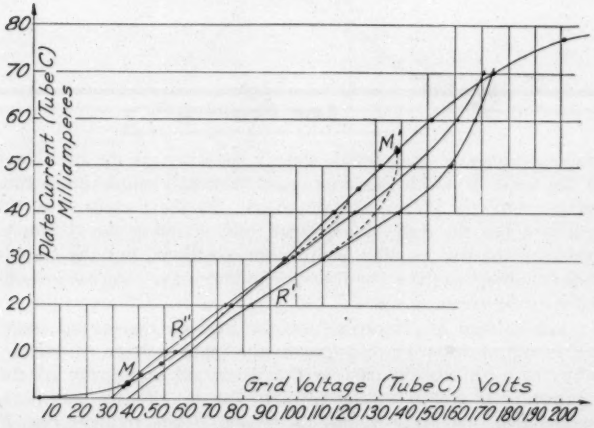
The above study was made under the assumption that:

(1) The potentiometer circuit follows Ohm's law.

(2) The second tube B works substantially on the rectilinear part of its characteristic.

In case one or both of the above conditions is not fulfilled,

FIG. 9.



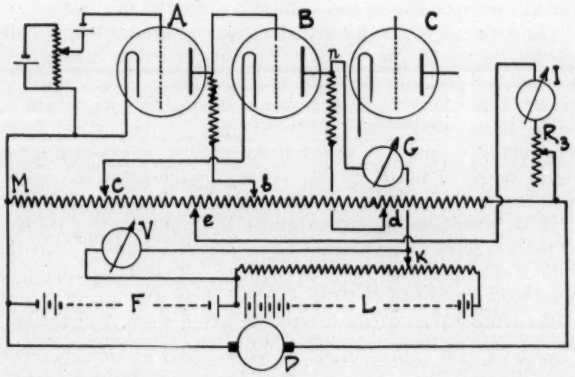
instead of a straight line, the receiver characteristic R can be a curve. Kaufmann's criterion permits, however, to proceed in exactly the same manner as before. Fig. 9 represents the curves

obtained in the case of a potentiometer made of three carbon lamps (nearest to the negative terminal of the generator), and ten Mazda lamps, all in series. The shape of the R curve is due to the superposition of a number of partial characteristics (curvature of the characteristic of the second tube B, Mazda lamps have a positive, and carbon lamps a negative temperature coefficient, etc.) of the various parts of the circuit. To move the receiver curve from R to R' and *vice versa*, about 10–20 millivolts are necessary on the grid of the first tube. Point M corresponds to the first position R, and M' of the curve corresponds to the second position R'. Both points correspond to the stable equilibrium of the system, but their relative position is widely different, and corresponds nearly to 40 milliamperes; that is, practically to the full swing on the two 101D tubes constituting the last stage C.

7. EXPERIMENTAL CHECK OF THE CONDITIONS OF STABILITY.

The scheme shown on Fig. 10 represents the arrangement used to take experimentally the R curves of the circuit. For

FIG. 10.



this purpose, tube C was removed, and a variable resistor R_3 was connected across its terminals (e and f). (The resistance of R_3 could be varied within the same limits as the plate to filament resistance of C varies under the test.) The current I

through the resistor R_3 was made to vary by equal amounts (every 10 milliamperes) and to each value of I a corresponding value of the potential of point n was measured. The last-mentioned operation was performed by means of a zero method; a 130-volt dry-cell battery F was connected by its negative pole to the negative end of the generator D. In series with it there was a 90-volt storage battery L with a potentiometer across its terminals; the movable point K of the potentiometer was displaced until, for a given value of I, the galvanometer G would come to zero, indicating thus the equality of potentials of the points n and k, respectively. The potential of point k was measured by means of an ordinary voltmeter.

In order to take the G curve of the same circuit, the resistor R_3 was removed, and the tubes C substituted for it. The grids of the tubes C were connected, in this case, directly to point k of the potentiometer. The two R curves (Fig. 9) were taken for two values of the potential on the grid of the first tube A, namely, for $V'_g = 1.830$, and $V''_g = 1.836$ volts, respectively. The two R curves corresponding to these values are indicated as R' and R''. The R curves thus obtained represent the static R curves corresponding to the zero method used in this test.

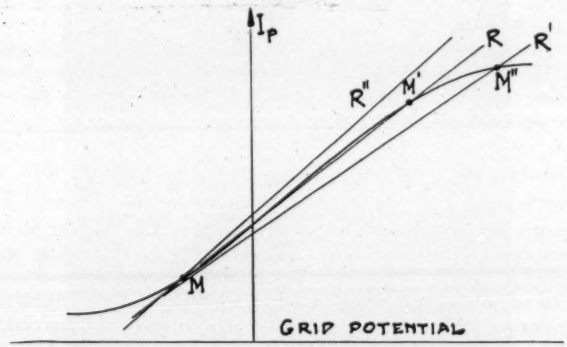
In order to obtain the actual R curve corresponding to the scheme shown on Fig. 1, an additional correction, taking into account the grid current I_g flowing into the C tubes, must be made. This additional drop in voltage is equal to $I_g R_2$, where R_2 is the resistance in series with the plate of the second stage. The curves R'_1 and R''_1, shown in dotted lines, represent the corrected values of the R curves. Thus, for the curve R''_1 corresponding to $V''_g = 1.836$ volts, the only point of stable equilibrium is at M, corresponding approximately to 5 milliamperes (output of the last tubes C); for $V'_g = 1.830$ volts the curve R'_1 has the only stable point at M', as this is apparent by applying Kaufmann's criterion to those points. These data are very close to the actual values of the currents observed when the phenomenon of self-excitation takes place in the scheme shown on Fig. 1.

8. DYNAMICAL CHARACTERISTICS, CRITICAL CONDITIONS.

The above-described conditions of stability correspond to a steady state. They are applicable when the potential of the grid of the first stage is just outside of the critical zone DC

(see Fig. 2), in which the phenomenon is erratic. The analysis of the phenomenon is more complicated inside this critical zone DC. The existence of this zone is due to the fact that within it the G and R curves have practically the same shape and can be made to coincide over a considerable range. Fig. 11 represents a condition of this kind. The R and G curves are shown to coincide at any point between M and M'. The equilibrium is, therefore, indifferent, in this case, between M and M', whereas these last-mentioned points themselves are the points of stability. This condition, however, is only theoretical, and, in practice, addi-

FIG. 11.



tional phenomena occur which, in some cases, may lead to peculiar oscillations which, in reality, are rather transients, corresponding to subsequent loss and recovery of stability. These phenomena are sometimes non-periodic (erratic), and sometimes they are periodic, according to the relative predominance of the various factors. These additional phenomena are due to the fact that the characteristics G and R of the system are not constant, but undergo slight changes (deformation, or displacement, or both), resulting from the transient itself. Thus, assume that the system has just reached momentarily the point M'' at which the equilibrium is stable, although the G and R curves have a very sharp intersection. The current through C has instantaneously increased during this change from M to M''. Due to this increase of the current the resistance of the metallic lamps goes up with

the current, and the R curve will swing from R' position to the position shown as R on Fig. 11, so that point M' thus reached becomes unstable. The plate current in C will fall abruptly to M, whereby the decrease of the resistance thus obtained will shift the receiver curve back to R' and oscillations will be thus started.

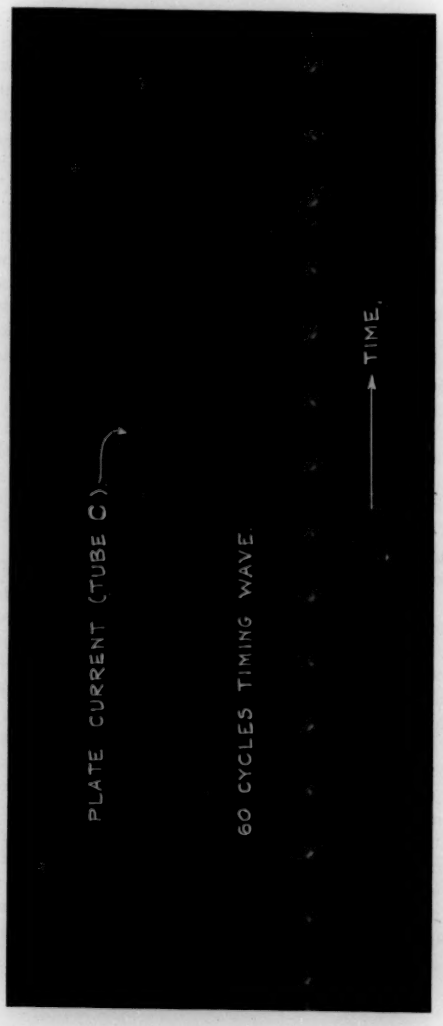
We can conveniently call these changes *dynamical*, and the instantaneous characteristics *dynamical* also to distinguish them from the statical curves introduced in the preliminary study of the phenomenon.

In the above example, the thermal phenomenon (variation of the resistance with heat) is the connecting link between the instantaneous value of the transient current and the dynamical value of the R curve.

This particular phenomenon is illustrated on the oscillogram No. 1, representing the plate current in the last tube plotted against the 60-cycle timing wave. The abrupt jumps in the current curve correspond to the instantaneous exchange of equilibrium between the points M'' and M as above explained. The time taken by this transient is very small as compared with the 60-cycle period; it is of the order of magnitude of $\frac{1}{2c0}$ sec. The phenomenon is not periodic in view of the fact that the above-mentioned thermal effects are not very regular, depending on a number of accidental causes such as air currents, etc.

In some cases, if the dynamical variations of the characteristic curves are caused by a periodic phenomenon and the system is very near the critical condition shown graphically on Fig. 11, the loss of stability may acquire a quasi-periodical character,|| that is, at a certain moment of the external periodic phenomenon, the transient is released and grows up according to its own law (generally an exponential law) which has nothing to do with the law of variation of the primary periodic external disturbance. If the frequency and the magnitude of the latter are sufficient to remove the original loss of equilibrium before the phenomenon gets out of the control, the direction of the transient phenomenon will be instantaneously reversed and will develop in the opposite direction.

|| We may designate the phenomenon as quasi-periodic when an essentially non-periodic transient is artificially reproduced by means of a suitable constraint. For more details, see C. P. Steinmetz, "Transient Electric Phenomena and Oscillations," pages 217–271, 1909 edition.



OSCILLOGRAM I.

The final effect will be periodic as the primary cause itself, causing the periodic oscillations of the dynamic curve G, R (see Fig. 11). This particular type of a quasi-periodic transient is shown on the oscillogram (No. 2) representing the plate current of the tube C (Fig. 1) plotted against 60-cycle timing wave. The oscillations in the dynamical characteristics are due to two distinct causes, both arising from the fact that the heating of the filaments is obtained by 60-cycle alternating current. The first cause is due to a purely electric effect of a slight oscillation of the potential of the filaments, because of a not quite symmetrical location of the middle point on the potentiometer; the second cause is due to a purely thermal effect (of double frequency) of variation of the filament temperature when heated by alternating current. The first cause is probably predominant, as the inspection of the oscillogram shows. Each curve has its own base line; the curve of the transient shows that it develops in the same direction always, as this might naturally be expected, in fact, the milliammeter in series with the plate of the C tube shows a steady deviation corresponding to the average value of the curve. Between the points a and b (oscillogram No. 2) there exists an equilibrium at the lower point M (Fig. 11), the dynamical curve being at the R'' position. At b this equilibrium is lost, the dynamic characteristic having passed through R to the R' position, which corresponds to the start of the transient. At C the R curve is again in R'', which corresponds to the only point of stability at M. The transient accordingly develops in the opposite direction, being of the nature of an ordinary exponential decay of current in an inductive circuit. The current in this test was very low, being only of the order of 5–10 milliamperes, corresponding thus to the part of the curve shown on Fig. 2, to the left from point D. During the time prior to A, oscillogram No. 3 represents exactly the same condition as shown on oscillogram No. 2, that is, a quasi-periodic transient, due to the periodic loss and recovery of equilibrium around point M of Fig. 11. At point A an additional D.-C. "trigger voltage" (about 30 millivolts) was introduced on the grid of tube A, which caused the displacement of the "R curve" from its position at R (Fig. 11) to R', to which a point of equilibrium at M'' corresponds. The transient is accordingly released (at point A of the oscillogram No. 3) and reaches steady value corresponding to M'' (Fig. 11) approxi-

OSCILLOGRAM 2.

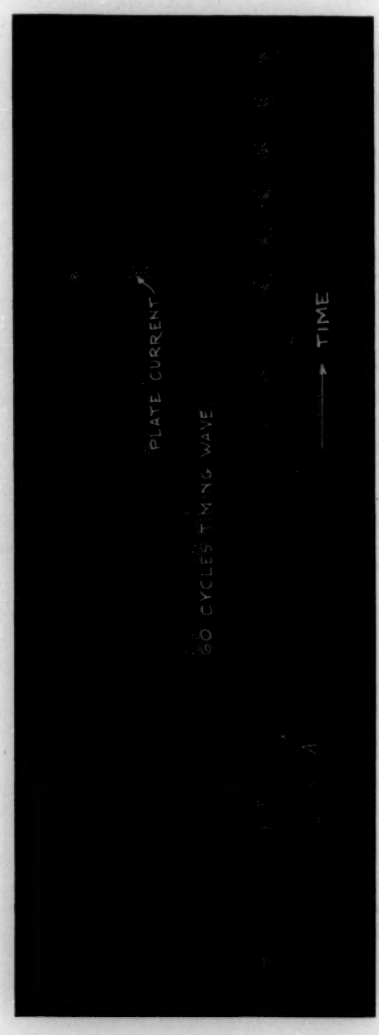
mately after a time of 1½ cycles frequency. It is interesting to note that a slight fluctuation is noticeable after the plate current has reached its steady value; the cause for this being the same as before (the effect of a slight variation of grid potential of the first tube *A*, due to A.-C. feeding of its filament), but its relative value is very small, since the dynamical oscillation of "curve *R*" occurs now around *R'* (and not around *R* as before) where the *R-G* curves cut each other at a greater angle.

9. COMPARISON BETWEEN THE VACUUM TUBE-CONTACT EFFECT SYSTEM AND THE EXISTING APPARATUS (RELAYS, CONTACTORS).

It is interesting to compare the facilities afforded by the new phenomenon which we have designated as contact effect with the ordinary electromagnetically operated material contacts in all kinds of relays, contactors, etc.

The first important difference is in the fact that the new phenomenon affords facility for making or breaking a current without any material contacts, which would be subject to deterioration. Oscillogram No. 4 represents "the closing" of a current in a highly inductive circuit (field of a D.-C. generator), by means of the vacuum tube system shown on Fig. 1, occurring at instant *A* on the oscillogram. The current reaches approximately its full value after two periods of 60-cycle frequency. The ripple to the left of point *A* is due to the A.-C. feeding of the filaments in tubes *B* and *C* (Fig. 1); the filament of tube *A* was heated by a storage battery in this test. The jump of the current was from 1–2 milliamperes (before instant *A*) up to nearly 50 milliamperes.

The second important difference is due to the fact that, whereas the industrial devices such as relays, contactors, etc., are *electromagnetically operated* apparatus, the new scheme is *operated electrostatically*, which permits it to be operated by very small amounts of energy as compared with the amount of energy required to operate the devices of the first class. For instance, an industrial standard contactor closing a current of 10 amperes under 220 volts (that is, 2200 watts in power) will take probably something around 35 watts for its operation. If we designate conventionally as *power amplification* of a contactor the ratio $\frac{\text{power transmitted by the contactor}}{\text{operating power absorbed by the contactor}}$, in the above example this power amplification is $\frac{2200}{35}$ = about 63 times. Generally speaking,



OSCILLOGRAM 3.

the figure 100 : 1 seems to be the upper limit of power amplification by the existing industrial devices operated electromagnetically (order of magnitude $10^2 : 1$).

In the case of the contact effect in conditions in which the above oscillograms were taken, the change in the input voltage was about 40 millivolts and in the input (grid) current about 0.2 microampere. Thus the total power input absorbed by the electronic contactor was of the order of magnitude of 8×10^{-9} watts. As to the power transmitted in our case, it was about 2.5 watts. *The power amplification in this case was around* 3×10^8 *times; that is, about three million times greater in the existing industrial contactors.*

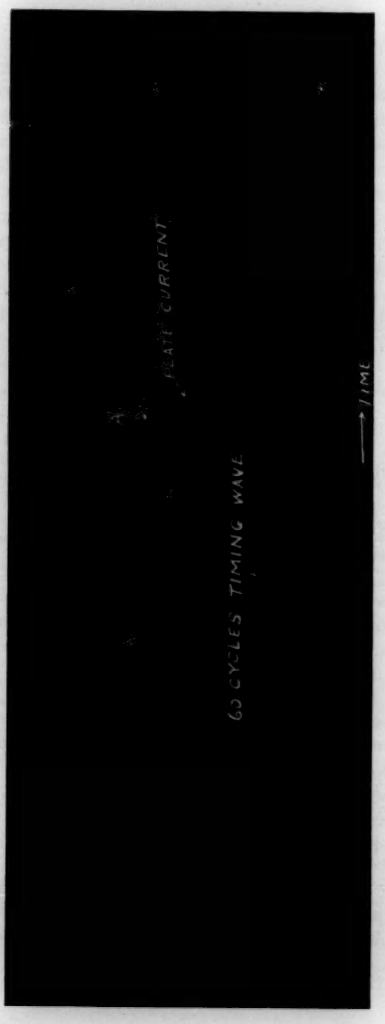
The above figures are not limiting; in fact, no attempt was made to increase the sensitiveness of the scheme when the oscillographic records were taken; on the contrary, it was intentionally lowered. Thus, for instance, instead of 40 millivolts of the trigger voltage, a 10 times smaller value could be obtained by a proper adjustment. The change in the grid current variation could be still further reduced by a proper biasing of the grid. Instead of 2.5 watts in the output, much greater change could be obtained by using power tubes, etc. *One sees, thus, that the power amplification of the new electronic relay can easily be made millions of times greater than that of the existing electromagnetically operated devices* with very simple means not requiring any ultra-sensitive devices or adjustments.

The above figures do not appear as extraordinary if one remembers that from the practical standpoint the new electronic relay utilizing the contact effect is operated *electrostatically*, which requires only very small amounts of energy.

A similar method of *electrostatic control* of power circuits was recently discovered by Dunoyer and Toulon,¶ who obtained a similar "contact effect" ** in a mercury arc controlled by the electrostatic action of an external sheath. The power amplification of the Dunoyer-Toulon scheme was of the order of magnitude of 10^{10}, that is, considerably higher than the order of magnitude for the power amplification ($10^6 : 1$ up to $10^8 : 1$)

¶ *Journal de Physique*, September and October issues, 1924.

** The authors of the above-cited paper use the expression "all or nothing" (in French: "tout ou rien") to designate the contact effect features of their scheme.



OSCILLOGRAM 4.

obtainable in our case. It must be remembered, however, that in the case of the Dunoyer-Toulon effect the control affects the power circuit directly (mercury arc of hundreds of amperes), whereas in our case it operates, so to say, upon *the excitation of the exciter*. If this circumstance is taken into consideration, the overall industrial power amplification of our scheme (that is, the ratio between the power released by the power installation to the power absorbed by the grid of the trigger tube) becomes easily of the order of magnitude $10^{10}:1$ up to possibly $10^{12}:1$, that is, approaches the Dunoyer figures. From the practical standpoint, each of these two schemes probably will have its own field of application. The Dunoyer scheme probably will be preferable whenever very large currents are to be controlled directly; on the other hand, the mercury arc as a switch is a rather expensive proposition; the loss in the arc, in fact, can easily reach several kilowatts. For industrial applications, such as voltage regulation of the power plants and similar uses where the exciters are being used now, this scheme probably will be more advantageous. Of course, the underlying physical phenomena in both cases are entirely different.

10. CONCLUSIONS.

The above-described phenomena of the contact effect represent a particular case of D.-C. self-excitation in the vacuum tube circuits. This particular condition in the vacuum tube system is characterized by the existence of two points of electrical stable equilibrium separated by a rather wide zone of instability.

The phenomenon can be controlled only on the edges of this zone of instability (which is very wide for the current to be controlled, but very narrow for the control voltage); the control, however, is lost inside the zone of instability where the phenomenon is governed exclusively by the transient of the readjustment between two stable states.

The vacuum tube system, connected as shown on Fig. 1, represents a special kind of *electrostatically controlled* relay with an enormous power amplification ($10^6:1$ up to $10^8:1$) which can be utilized for many practical purposes. In fact, it bridges, so to say, the gap between the infinitely small (in a practical sense) and finite amounts of energy between the ergs and the kilowatts by a simple electric circuit without any complicated mechanical

refinements, and without any sparking contacts subject to deterioration.

The applications of this new "electronic contactor," it is hoped, will appeal both to the common sense of the industrial engineer and to the creative imagination of the inventor by the possibility to make ergs to control kilowatts in a very simple and reliable manner.

In conclusion, the writer wishes to acknowledge his thanks to Dr. H. Pender, the Dean of this school, for his interest and encouragement of this research as well as for the facilities afforded for its prosecution by the recently organized Research Laboratory of the Moore School in which this work was conducted.

Thanks are acknowledged also to the Staff of the Moore School for its friendly coöperation in this work. The writer is particularly indebted to Assistant Professor R. E. Brown and to the school's mechanic, Mr. M. E. Nelson, for valuable help, especially in the oscillographic work.

On the Change of Refractive Index of Linseed Oil in the Process of Drying and Its Effect on the Deterioration of Oil Paintings. A. P. LAURIE. (*Proc. Roy. Soc.*, A 760.)—The Royal Academy has a committee appointed to examine the durability of paintings. This paper is a report of work undertaken to furnish information to it. Modern oil pictures after the lapse of years show a lowering of tone over the entire surface, in this respect differing from the early fifteenth-century paintings in oil and from later Dutch products. "As the medium—linseed, walnut or poppy oil—is the same, and as the modern painter uses in many cases the same pigments, and in other cases superior substitutes, the cause of this lowering of tone must be found rather in the unscientific methods of using the materials than in materials themselves. This view is confirmed by the fact that an examination of modern pictures—by which I mean pictures painted in the last hundred years—reveals marked differences in the extent to which lowering of tone has taken place. The pigments, if properly selected, being permanent under the conditions in a picture gallery, the lowering of tone must be ascribed to the medium."

Oxidized films of the oils mentioned above turn yellow with age, though linseed oil shows this change most markedly. This yellowing affects the red and yellow pigments less than those at the other end of the spectrum. A transparent pigment such as cobalt blue is more affected than an opaque pigment. The author cites a case where cobalt blue in oil had turned black after forty years in a studio. A

few weeks' exposure at the window bleached the oil and brought back the blue color.

We may consider pigments as transparent substances of high refractive indices. When they are in a medium, the quantity of light reflected at the surface of the pigments depends in part upon the relation between the indices of refraction of the medium and pigment. The less this difference, the larger the fraction of light penetrating the pigment and the smaller the part reflected. This accounts for the following: "A chrome yellow, for instance, becomes deeper in tone and less brilliant when air is replaced by water, and still more deep and lowered in tone when water is replaced by oil." The author ground a number of common pigments used by artists in media of high refractive indices, bromo-naphthalene, 1.65, and methylene-iodide saturated with sulphur, 1.8. White lead ground in the former appeared as a grayish translucent powder, consisting of transparent, doubly refracting crystals. He arranges the pigments of a given color in order, the first being those that appear transparent in linseed oil and the last that which remains opaque in the medium of highest refractive index.

The change of refractive index as linseed oil ages was investigated. In three days the value of the index increased from 1.48 to 1.49. In eight months it rose from 1.492 to 1.50. "A change in refractive index from 1.480 to 1.500 causes a perceptible degradation of tone in white lead and makes a pale cadmium yellow appear dull and more orange in tint." The methods of painting in the time of the Van Eycks and later are described and the conclusion is drawn that they made the effect of yellowing neutralize the effect of increase of index of refraction. "The painters of that time had thoroughly mastered the possibilities of the oil film, both in the matter of yellowing and of change of refractive index, and there can be no question that under modern conditions of painting in oil, the neglect of these two factors is the explanation of the lowering of tone which so often takes place." G. F. S.

Fat Content of Malted Milk.—The quantitative determination of the fat content of malted milk is a difficult and tedious process, yielding uncertain results. EDWARD S. ROSE (*Am. J. Phar.*, 1926, **98**, 595–596), who has made a study of the various proposed methods, recommends the following procedure. The malted milk (0.5 to 1.0 gram) is mixed with 5 c.c. of hot water and 10 c.c. of concentrated hydrochloric acid; the mixture is heated in a bath of boiling water for five minutes, then is cooled, and extracted by shaking for two minutes with 25 to 30 c.c. of a mixture of one volume of washed ether and two volumes of benzin, U. S. P. The extraction is repeated twice with new portions of the solvent. The extracts are combined in a tarred flask; the solvents are removed by evaporation; and the mass of the fat is obtained after drying to constant weight. J. S. H.

A CRITICAL SURVEY OF SOME RECENT ADVANCES IN THE STUDY OF DIAMAGNETISM.*

BY

E. S. BIELER, Ph.D.

Assistant Professor of Physics, McGill University.

I. INTRODUCTION.

THIS article is the outcome of a Graduate School Colloquium delivered at McGill University during the Session 1925–1926. After a thorough search of the literature, the writer came to the conclusion that there was room for a fuller account in English of the subject of diamagnetism, bringing together not only the fundamental theoretical work of Langevin, and the large amount of experimental work that has been carried out before and since, but trying at the same time to connect up the occurrence of diamagnetic properties in elements and compounds with the remarkable work of Bohr and his followers on the periodic system of the elements.

On consulting a table of susceptibilities, such as the one given by Landolt and Börnstein,[1] one cannot help being struck by the great prevalence of diamagnetic properties among elements and compounds. About half the elements in the periodic table are what we may term *diamagnetic*. By this, we mean that all the saturated compounds which they form with each other are diamagnetic, although the elements themselves may show paramagnetism in the free state. In addition, even such elements as iron or nickel form many complex salts which are actually diamagnetic.

Diamagnetism, being such a common property of matter, is well worth studying for itself. But the magnetic properties of substances are very closely connected with the way in which their atoms are bound together. Iron, for instance, which is very strongly magnetic in the metallic form, actually forms some compounds which are diamagnetic. A study of diamagnetism therefore cannot fail to throw a great deal of light on the structure of atoms, and on the way in which this structure is altered when an atom enters into combination.

Our knowledge of the magnetic properties of atoms has

* Communicated by the Author.

increased very greatly in the last few years. On the one hand, the experiments of Gerlach and Stern,[25] on the deflection of streams of uncharged atoms in a non-uniform magnetic field, have made possible the study of the magnetic properties of the isolated atom. On the other hand, the theoretical work of Landé, Sommerfeld, and others, has enabled us to interpret the peculiarities of atomic spectra in a magnetic field, particularly the anomalous Zeeman effect in terms of the distribution and orientation of electronic orbits.

The object of this article is to review the more important results which have been obtained on diamagnetism, and the classification which has been made of them, and to examine them in terms of our present knowledge of the atom, and of the way in which it enters into combination with other atoms. Owing probably to the greater variety of phenomena connected with paramagnetism and ferromagnetism, only a small place seems to have been accorded to diamagnetism in most monographs. But, owing to its very fundamental nature, diamagnetism seems to deserve a more ample treatment. This article is an attempt to supply this want.

In this connection, the writer desires to mention a recent review of magnetism due to B. Cabrera[2]: "Le Magnétisme et la Structure de l'Atome et de la Molécule." The first article, which did not reach the writer until this survey was nearly completed, is very largely concerned with diamagnetism.

The present survey does not aim at completeness. The writer has tried to bring together significant facts and to examine them in the light of modern theories of atomic constitution. In doing so, he has tried to lay emphasis on the points which seem to him unsatisfactory in the present theory, and on the directions in which further experimental work on the subject would seem to be indicated. If he succeeds in drawing the attention of a few to the importance of the subject, he will deem himself well repaid for his effort.

II. DIAMAGNETISM AND THE LARMOR ROTATION.

We can date the beginning of the modern theory of diamagnetism to Langevin's paper, "Magnétisme et Théorie des Electrons,"[3] published in 1905.

Langevin showed that a "magnetic molecule" consisting of

a spherically symmetrical distribution of electrical charges, either at rest or in orbital motion, had no tendency to orient itself in any particular direction with respect to a magnetic field, but would begin to rotate with a definite angular velocity round the lines of magnetic force. This angular velocity, which has been called the Larmor rotation, is given by

$$\omega = -\frac{e}{2mc} \cdot H \tag{1}$$

where e/m is the ratio of charge to mass of the electron on the electrostatic system, c is the velocity of light, and H the field in gausses.

On the basis of the present-day conception of the nuclear atom, it is natural to identify this atom with Langevin's "magnetic molecule." The theory holds then in exactly the same way for such atoms as possess some sort of spherical symmetry, whether we adopt the Lewis-Langmuir static model or the Bohr dynamical model, provided we assume both models to have sufficient rigidity not to be distorted by the magnetic field.

Now, an electron at distance r from an axis, revolving with angular velocity ω round that axis gives rise to a magnetic moment given by

$$\delta M = \frac{e}{c} \cdot \frac{\omega}{2\pi} \cdot \pi r^2 = \frac{e\omega r^2}{2c}$$

$$= -\frac{e}{4mc^2} \cdot er^2 \cdot H \tag{2}$$

when we have substituted for ω the value given by (1).

If the atom contains several electrons, the total magnetic moment M_a of the atom is given by

$$M_a = -\frac{e}{4mc^2} \cdot \Sigma er^2 \cdot H. \tag{3}$$

Now, owing to the spherical symmetry of the diamagnetic atom, we have,

$$\Sigma er^2 = \frac{2}{3} \Sigma eR^2 \tag{4}$$

where r refers to the distance of the typical electron from the axis of rotation through the nucleus, and R refers to its distance from the nucleus itself.

Thus,

$$M_a = -\frac{e}{6mc^2} \cdot \Sigma eR^2 \cdot H \tag{5}$$

The magnetic moment per gram-molecule is therefore

$$M_m = -L \cdot \frac{e}{6mc^2} \cdot \Sigma eR^2 \cdot H \tag{6}$$

where L is Avogadro's number, 6.06×10^{23} molecules per gram-molecule; and I, the magnetic moment per unit volume, or intensity of magnetization, is given by

$$I = M_v = -L \cdot \frac{d}{A} \cdot \frac{e}{6mc^2} \cdot \Sigma eR^2 \cdot H \tag{7}$$

where d is the density of the substance, and A the atomic weight.

The susceptibility is therefore

$$\kappa_v = \frac{I}{H} = -L \cdot \frac{d}{A} \cdot \frac{e}{6mc^2} \cdot \Sigma eR^2. \tag{8}$$

The so-called "atomic susceptibility," or susceptibility which the substance would possess if one gram-molecule of it were concentrated within unit volume, is, therefore,

$$\chi = \frac{M_m}{H} = -L \cdot \frac{e}{6mc^2} \cdot \Sigma eR^2. \tag{9}$$

This is the susceptibility most conveniently used in theoretical work, and it is very easily obtained from the volume susceptibility by the relation

$$\kappa_v = \frac{d}{A} \cdot \chi. \tag{10}$$

Another constant often used in defining susceptibility is the so-called "mass susceptibility," κ_m, connected with κ_v by the relation,

$$\kappa_v = d \cdot \kappa_m. \tag{11}$$

III. MODERN VIEWS ON THE ELECTRONIC STRUCTURE OF THE ATOM.

It is impossible to discuss the application of the Langevin theory of diamagnetism to the atom without recalling the ideas of Bohr and his followers on the relation between the properties of the elements and their electron structure. Two recent contributions, due to Stoner[4] and Pauli,[5] have so sharpened Bohr's original ideas as to afford a very definite basis on which to discuss the magnetic properties of the atom.

There are few essays on subjects in modern physics which are more suggestive of explanations of known phenomena, and of ideas for further work than the third part of a book recently published by Niels Bohr[6] on "The Theory of Spectra and

Atomic Constitution." In this third part, entitled "Physical and Chemical Properties of the Elements," the Danish physicist brings together for the first time all the main phenomena which must be explained quantitatively by any satisfactory theory of atomic structure, and these I would put down under three heads:

(*a*) Periodicity of chemical properties and of type of optical spectra throughout the periodic table.

(*b*) Appearance of well-defined paramagnetic character, and of characteristic colors in compounds at definite places in certain periods.

(*c*) Gradual increase of X-ray frequencies throughout the table.

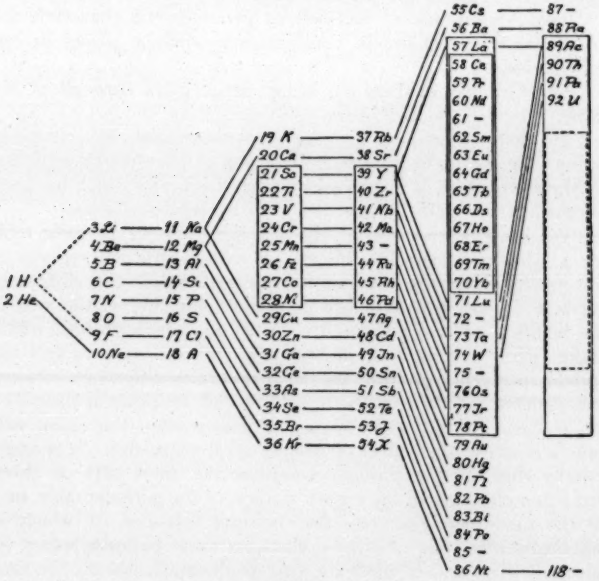
He then proceeds to develop from these facts as a starting-point a theory of the gradual building up of the electron structure of the atom which is in agreement with them, and which has been adopted in the main by practically all modern physicists.

We have reproduced in Fig. 1 a form of the periodic table on which Bohr bases his theory. Except within the regions of the table which are surrounded by rectangles, the difference between the electron structure of one element and of the next is the addition of one electron to one of the outer groups, which makes itself felt at once in both the chemical valence and the optical spectrum. Within the rectangles, the difference between one element and the next is the addition of an electron to one of the electron groups which, being already within the atom, will have a much smaller effect on the chemical properties. It is noteworthy that these rectangles comprise the three sets of three transition elements of the eighth column of the periodic table, and all the rare-earth elements, the chemical behavior of which is practically identical. All these elements show paramagnetism in the pure form and in most of their compounds, due to the fact that they contain an incomplete, and therefore unsymmetrical group of electron orbits, which cannot be completed by chemical combination because it is some way within the structure of the atom. They also show characteristic colors in their salts, due to the fact that the small amount of energy absorbed from certain regions of the visible spectrum is sufficient to cause some internal rearrangement of the uncompleted group.

An examination of a table of susceptibilities of elements and compounds, like that given by Landolt and Börnstein,[1] will show

at once that saturated compounds of the elements outside of the rectangles of Fig. 1 are practically all diamagnetic, whereas nearly all compounds containing elements within the rectangles are paramagnetic. The diamagnetic compounds of these latter elements will be dealt with in the next section. We shall call the elements

FIG. 1.



The periodic table, according to Bohr.

outside the rectangles "*diamagnetic elements*," the others "*paramagnetic elements*."

Bohr's scheme for the explanation of the periodic table was based on the assumption of only two quantum numbers for each electron orbit, namely, the total quantum number n, and the azimuthal quantum number k, both of which were supposed integral.

A consideration of the multiplet structure of optical and X-ray lines, however, showed that it is necessary to assume a third

quantum number j to account for it. Stoner's [4] contribution to the theory was to redistribute the electrons among the possible orbits, as defined by the three quantum numbers (n, k, j). By making the very simple assumption that *the number of electrons in any one group is equal to twice the inner quantum number of that group,* he was able to evolve a scheme for the gradual building up of the electronic shell throughout the periodic table, in which each group of electrons is completed before the building up of the next group begins. This arrangement was much more satisfactory than Bohr's from the point of view of intensities of optical and X-ray lines.

The latest improvement in the theory of the building up of the electronic structure of the atom is due to the German physicist, Pauli.[5] His allotment of electrons to each electron group is exactly the same as Stoner's, but the designation of the groups is rather different, and each is further subdivided by the introduction of a fourth quantum number, m_1, rendered necessary by the consideration of the anomalous Zeeman effect. Up to the present, the theory seems to have mainly a formal character, but it furnishes a very striking explanation of the occurrence of *complete electron groups* containing 2, 8, 18, and 32 electrons, and of the fact that *such groups do not possess a magnetic axis,* and it seems that it can be extended to apply to the diamagnetism of other less symmetrical groupings.

Pauli considers an electron orbit in a magnetic field to be defined by four quantum numbers, the total quantum number, n, the azimuthal quantum number k_1, the "effective" quantum number k_2, all of which are integral, and lastly the magnetic quantum number m_1, which is always half an odd integer. The magnetic quantum number defines the contribution of the electron orbit to the magnetic moment of the atom.

Pauli then assumes that, *in a given atom, there can be only one electron in each of the possible orbits,* that is, only one electron can have a given combination of the four quantum numbers. Having assigned the values of k_1, k_2, and m_1, which, according to spectroscopic evidence can be associated with a given value of n, he is then able to say how many electrons there can be in the group whose total quantum number is n. Of course, as in the original Bohr theory of the building up of the electronic structure, those orbits will be first established which are most tightly bound.

Table I gives the scheme of quantum numbers which Pauli adopts for $n = 1, 2, 3$, and 4, and the number of possible combinations, which is equal to the number of electrons in each completed group.

Pauli's ideas as to the distribution of electrons among the possible orbits have the following very distinct advantages:

(*a*) They afford a simple explanation of the occurrence of completed electron groups in atoms, containing 2, 8, 18, 32 electrons. Reference to Table I will indicate at once that the number

TABLE I.

Number of Electrons in the Various Groups According to Pauli.

Group.	*K.*	*L.*		*M.*				
n	1	2		3				
k_1	1	1	2	1	2		3	
k_2	1	1	2	1	1	2	2	3
m_1	$\pm\frac{1}{2}$	$\pm\frac{1}{2}$	$\pm\frac{1}{2}, \pm\frac{3}{2}$	$\pm\frac{1}{2}$	$\pm\frac{1}{2}$	$\pm\frac{1}{2}, \pm\frac{3}{2}$	$\pm\frac{1}{2}, \pm\frac{3}{2}$	$\pm\frac{1}{2}, \pm\frac{3}{2}, \pm\frac{5}{2}$
Number of Combinations	2	2	+2 +4	2	+2	+4	+4	+6
	$=2.1^2$	$=8$	$=2.2^2$	$=18=2.3^2$				

Group.	*N.*									
n	4									
k_1	1	2		3			4			
k_2	1	1	2	2	3		3	4		
m_1	$\pm\frac{1}{2}$	$\pm\frac{1}{2}$	$\pm\frac{1}{2}, \pm\frac{3}{2}$	$\pm\frac{1}{2}, \pm\frac{3}{2}$	$\pm\frac{1}{2}, \pm\frac{3}{2}, \pm\frac{5}{2}$		$\pm\frac{1}{2}, \pm\frac{3}{2}, \pm\frac{5}{2}$	$\pm\frac{1}{2}, \pm\frac{3}{2}, \pm\frac{5}{2}, \pm\frac{7}{2}$		
Number of Combinations	2	+2	+4	+4	+6		+6	+8		
				$=32$	$=2.4^2$					

of electrons in a completed group of quantum number n is $2.n^2$.

(*b*) They give a very reasonable basis for Stoner's assumption that the number of electrons in a completed (n, k, j) group is twice the quantum number j of the group. According to Pauli, only one electron can be in any one orbit and the number of possible orbits, given by the number of possible combinations of the four quantum numbers (n, k_1, k_2, m_1) is exactly that which is assumed by Stoner, and shown by him to be in accordance with experimental data on the intensities of optical and X-ray lines.

(*c*) At the hands of Hund[7] they have already made possible the coördination of a large number of complex spectra, and have

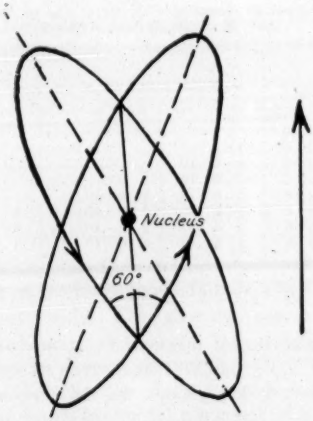
furnished a formal explanation of the paramagnetism of the rare earths.

We shall show in the following sections that Pauli's theory is also in good agreement with data on the magnetic properties of atoms, whether isolated or associated with other atoms.

IV. THE SYMMETRICAL ELECTRON STRUCTURES AND DIAMAGNETISM.

(*a*) THE INERT GASES AND THE IONS CU^+, AG^+ AND AU^+.
(*b*) IONS IN SOLUTIONS AND SALT CRYSTALS.
(*c*) CALCULATION OF DIAMAGNETISM FROM DIMENSIONS OF ELECTRON ORBITS.

FIG. 2.



Landé's model of the helium atom.

(*a*) *The Inert Gases and the Ions Cu⁺, Ag⁺ and Au⁺.*—The electronic structure of the inert gases has long been known to possess a very high degree of symmetry, and it is naturally to them that one would turn first to test a theory of diamagnetism based on electrical symmetry. On Bohr's original theory, it was extremely difficult to understand how the magnetic moments due to the various electrons would counterbalance each other so that the whole atom possessed no resultant magnetic moment. To take a very simple case, that of He, the well-known Landé model

consisting of two electrons in approximately circular orbits at 120° to each other would be expected to have a very definite magnetic moment in the direction of the arrow (Fig. 2).

On Pauli's present ideas, however, in the presence of a magnetic field, the two electrons will be in $\left(1, 1, 1, +\frac{1}{2}\right)$ and $\left(1, 1, 1, -\frac{1}{2}\right)$ orbits (Table I). The magnetic quantum number m_1 is $+\frac{1}{2}$ for one electron, $-\frac{1}{2}$ for the other, and the total magnetic moment is nil. Physically this must be interpreted in terms of a precession of each orbit with respect to the magnetic field of the

TABLE II.

Distribution of Electrons in Atoms of Rare Gases and in the Ions Cu^+, Ag^+, Au^+, According to Pauli's Theory.

n	1	2		3			4				5			6	
k_1	1	1	2	1	2	3	1	2	3	4	1	2	3	1	2
2He	2														
10Ne	2	2	6												
18A	2	2	6	2	6										
$28Cu^+$	2	2	6	2	6	10									
36Kr	2	2	6	2	6	10	2	6							
$46Ag^+$	2	2	6	2	6	10	2	6	10						
54Xe	2	2	6	2	6	10	2	6	10		2	6			
$78Au^+$	2	2	6	2	6	10	2	6	10	14	2	6	10		
86Rn	2	2	6	2	6	10	2	6	10	14	2	6	10	2	6

same amount, but opposite direction, so that the two annul each other.

The same balancing of magnetic contributions will occur in any complete (n, k_1) group, so that electron structures consisting only of complete (n, k_1) groups will have no resultant magnetic moment.

This is the case, not only for the rare gases, but also among others, for three configurations of almost equal importance in a consideration of the periodic table, namely, those of the ions. Cu^+, Ag^+ and Au^+. Table II gives the allotments of electrons to the various (n, k_1) groups in these configurations.

Of these structures only those of the inert gases are stable under the attraction of a positive nuclear charge equal to their own negative charge. Of the others, Ag^+ is definitely stable under the attraction of a nuclear charge of +47, as the strictly monovalent character of Ag and the lack of color in its simple

salts indicate.† The Cu^{+} and Au^{+} distributions seem to be capable of existence under nuclear charges 29 and 79, respectively, but the fact that Cu^{++} and Au^{+++} occur more often in combination proves that these distributions are not stable.‡ It is only in Zn^{++} and Hg^{++} that they seem to reach their full stability.

The first definite attempt to apply Langevin's theory quantitatively to the diamagnetism of the rare gases seems to have been that of Pauli.[8] From very simple notions about atomic dimensions, he calculated a value of ΣeR^2 for A and He, and proved definitely that the experimental results of Tänzler [9] and Také Soné [10] indicated an atomic susceptibility far greater than any reasonable theory would allow.

The very careful measurements of Hector,[11] using a sensitive magnetic balance method developed by Wills,[12] have shown that

TABLE III.

Susceptibility of Inert Gases (Wills and Hector).

Element.	$\kappa_\rho \times 10^{10}$	$\chi \times 10^{6}$	$\Sigma eR^2 \times 10^{26}$
He	0.780	1.87	3.14
Ne	2.77	6.62	11.1
A	7.52	18.0	30.2

Pauli's theoretical deductions were correct, and that the atomic susceptibilities of the inert gases are only about one-tenth of the values found previously. They gave the values for He, Ne and A given in Table III.

In spite of the general agreement with Pauli's calculations, the writer is still inclined to think that the value for He is far too high. Taking an He model composed of a nucleus and two electrons rotating in the same orbit so as to be always at the end of a diameter, one obtains by a very simple calculation, for the radius of the orbit in He.

$$a_{He} = \frac{4}{7} a_H = 0.3 \times 10^{-8} \text{ cm.}$$

† Spectrum considerations indicate that the structure is stable even under a nuclear charge of +46 as in the neutral Pd atom. See McLennan, McLay and Smith, *Proc. Roy. Soc.*, **A**, 112, p. 76 (Aug. 3, 1926).

‡ My attention has been drawn by Mr. E. C. Stoner to the fact that spectroscopic considerations point to exactly the same conclusion. See Grimm and Sommerfeld, *Zeits. f. Phys.*, 36, p. 36 (1926).

where $a_H = 0.53 \times 10^{-8}$ cm., the radius of the orbit of the electron in H when in the lowest energy level.

This gives at once

$$\Sigma eR^2 = 2 \times 4.77 \times 10^{-10} \times (0.3 \times 10^{-8})^2 = 0.86 \times 10^{-26},$$

a value equal to about one-fourth of Hector's value. Of course, the above model would not be diamagnetic, but the dimensions of a diamagnetic model cannot be very different.

(*b*) *Ions in Solutions and Salt Crystals.*—The application of Langevin's theory to inert gases has not so far been tested directly in other cases. It has, however, been abundantly tested in the case of very similar electronic structures, namely, ions in solutions and in salt crystals.

Joos [13] was the first to apply the Langevin theory definitely to solutions of the alkali halides. In solution, these salts are dissociated into alkali ions with a single positive charge and halogen ions with a single negative charge. These possess exactly the same number of electrons as members of the inert gas series and presumably the same electronic configuration. To take a concrete case, a solution of KCl will contain K^+ ions and Cl^- ions both with eighteen electrons, the same number as in the inert gas A which falls between Cl and K in the periodic table. Owing to its larger nuclear charge (+19), the K^+ ions will be smaller than the Cl^- ions with nuclear charge +17. Joos makes the assumption that the linear dimensions of the electronic system are inversely proportional to the nuclear charge, and that the susceptibility is therefore inversely as the square of the charge.

Basing himself on the measurements carried out by Koenigsberger [14] on solutions of the alkali halides, and dividing the observed susceptibility between the ions on the above basis,

TABLE IV.

Atomic Susceptibilities of Ions $\times 10^6$.

No. of Electrons.	2	8	18	36	54
Halogens.....		F^- −11.5	Cl^- −19.5	Br^- −39.5	I^- −60.5
Inert Gases.....		Ne (− 8.7)	A (−16.8)		
Alkalies.....	$Li^+ > 0$	Na^+ − 6.5	K^+ −14.5		

Joos obtained the values given in Table IV for the susceptibilities of the ions.

The values for the inert gases are interpolated by the writer

between those for ions of like structure. It will be seen that they agree very well with Hector's experimental values. Joos ascribes the apparent paramagnetic susceptibility of the Li^+ ion to a distortion it may cause in the water molecule.

In just the same way, calculations of atomic susceptibility can be made from observations on alkali halides in the solid form, or on the mono-halides of Cu, Ag, and Au. There is every indication that the same ionic form is preserved as in the solutions, so that the observed diamagnetism can be ascribed to the Larmor rotation of symmetrical electronic distributions as in the inert gases and in solutions.

The atomic susceptibilities calculated from measurements on solid salts are usually slightly lower than those calculated from measurements on solutions. This may be due to a slight compression of the electronic structure in solid salts due to electrostatic attraction between neighboring ions.

Such a calculation has lately been carried out by Miss Crow [15] to determine the susceptibility of the rare gases Kr and Xe from measurements on the susceptibility of RbBr, and CsI, two salts

TABLE V.

Atomic Susceptibility of Krypton and Xenon $\times 10^6$ (*Miss Crow*).

No. of Electrons.	36		54	
Halogens	Br^-	−33.0	I^-	−40.2
Inert Gases	Kr	−31.5	Xe	−38.8
Alkalies	Rb^+	−29.9	Cs^+	−37.4

which bear to Kr and Xe exactly the same relation that KCl bears to A. She obtained the results given in Table V.

(*c*) *Calculation of Diamagnetism from Dimensions of Electron Orbits.*—Not only are the susceptibilities of ions in halogens halide structures of the order that one might expect from the general dimensions of the ions. In one case at least, that of NaCl, it is possible to compare the susceptibility determined directly with that calculated from experimental data on the distances of electrons from the Na and Cl nuclei. These data were obtained by Bragg, James and Bosanquet [16] in experiments on the intensity of the X-ray reflection from the various planes in a crystal of the salt.

Since the reflection is really a scattering from the electrons in each atom, there are differences of phase between the wavelets scattered by the various electrons in the atom, and consequently a variation of the intensity of the reflected wave made up of these according to the angle between the incident X-ray and the crystal plane producing the reflection.

These workers found that the electron distribution which gave the best fit to the experimental results was the following:

Sodium.

7 electrons on a shell of radius 0.29 Å.
3 electrons on a shell of radius 0.76 Å.

Chlorine.

10 electrons on a shell of radius 0.25 Å.
5 electrons on a shell of radius 0.86 Å.
3 electrons on a shell of radius 1.46 Å.

Of course, they do not claim that the electrons are actually fixed or revolving at distances equal to these. The numbers only represent a time average of the number of electrons whose mean distance from the nucleus is the above.

If we calculate ΣR^2 from these figures, we obtain, for Na, 2.54×10^{-16} sq. cm. and for Cl, 10.46×10^{-16} sq. cm.

This gives the following atomic susceptibilities, if we make use of equation (9): For Na, -7.2×10^{-6}; Cl, -29.8×10^{-6}.

Considering the difficulty of the X-ray measurement, the agreement with the values of Table IV is quite satisfactory.

It would be very interesting to carry out calculations of susceptibilities based on the dimensions of electronic orbits obtained by D. R. Hartree [17] from data of optical and X-ray levels. The writer hopes to have these carried out here in the near future.

V. THE EXPERIMENTAL EVIDENCE ON THE SUSCEPTIBILITY OF DIAMAGNETIC ELEMENTS AND THEIR COMPOUNDS.

As we have already pointed out, one cannot fail, on examining a table of susceptibilities such as that of Landolt and Börnstein,[1] to be struck with the very distinct diamagnetic character of the compounds of the elements which we have called "diamagnetic" elements, namely, those outside the rectangles of Fig. 1.

Thanks mainly to the very painstaking experimental work of

the French physical-chemist Pascal,[18] and to his very thorough comparative study of results, our knowledge of the susceptibility of diamagnetic elements has been quite satisfactorily systematized.

Pascal set out to investigate the question whether the diamagnetism of a compound could be determined from the characteristic susceptibility of the elements composing it. He concluded that, for any saturated compound, the molecular susceptibility χ_m can be set down in terms of the atomic susceptibility χ_a of the elements composing it by the formula,

$$\chi_m = \Sigma\chi_a + d,$$

where d is a quantity, positive, zero, or negative, which depends on the molecular constitution of the compound. The variation of this quantity d for various classes of compounds of the same element and for similar compounds of the elements of the same family, he has studied very thoroughly in the light of the older

TABLE VI.

Atomic Susceptibilities of Elements × 10^6. (*After Pascal.**)

Element.	At. No.	$-\chi \times 10^6$.	Element.	At. No.	$-\chi \times 10^6$.	Element.	At. No.	$-\chi \times 10^6$.
H	1	2.93	*Cl*	17	20.1	Ag	47	31.0
He	2	(1.87)H	A	18	(18.1)H	*Cd*	48	20.0
Li	3	4.20	K	19	18.5	In	49	15
Be	4	8.55	Ca	20	15.9	Sn^{IV}	50	30.3
B	5	7.30	Sc–Ni	21–28	Para	Sb^{III}	51	74.0
C	6	6.00	Cu	29	ca. 18	*Te*	52	37.5
N	7	5.57	Zn	30	13.5	*I*	53	44.6
O	8	4.61	*Ga*	31	16.8	Xe	54	(42.8)
F	9	5.95	Ge	32	.....	Cs	55	41.0
Ne	10	(6.6)H	As	33	43	Ba	56	38.2
Na	11	9.2	*Se*	34	23.1	La–Pt	58–78	Para
Mg	12	10.1	*Br*	35	30.5	*Au*	79	45.8
Al	13	ca. 13.2	Kr	36	(28.8)	Hg^{II}	80	33.4
Si	14	20.0	Rb	37	27.2	*Tl*	81	40.3
P	15	26.3	Sr	38	24.5	Pb	82	45.8
S	16	15.0	Y–Pd	39–46	Para	*Bi*	83	192

* *Comptes Rendus*, **158**, p. 1895, 1914.

theories of chemical valence, and he has brought out many very striking relations for which one must refer to his original papers.

After making the necessary corrections for the diamagnetic excess or deficiency d, Pascal has calculated the values given in Table VI for the atomic susceptibility of elements.

The values are all those given by Pascal, except for the rare

gases. The figures for He, Ne and A are from the measurements of Hector, those for Kr and X are interpolated between those of the two elements immediately preceding and following them. For the elements whose names have been printed in italics, the susceptibility has been found to be the same in the free and in the combined form. Pascal used measurements of his own,[18] as well as others due to Honda,[19] Owen,[20] and Koenigsberger.[14]

In Fig. 3, the logarithms of the atomic susceptibilities of Table VI have been plotted on a basis of atomic number. Pascal's original results were plotted on a basis of atomic weights. Two points are particularly striking in the curve: (1) The very definite similarity of the shape of the broken line in the various periods, except for elements below magnesium; (2) the fact that elements of the same group fall as a straight line.

In the figure, the straight lines have only been drawn for Group II and Group V. In the former, it is interesting to note that Mg falls in with Group II*b* (Zn, Cd, Hg) and not with Group II*a* (Ca, Sr, Ba).

VI. DISCUSSION OF EXPERIMENTAL EVIDENCE.

Table VI summarizes a large mass of experimental evidence as diamagnetism.

The discussion of these results will be taken up in this section, under three heads as follows:

(*a*) Diamagnetism in saturated compounds.
(*b*) Diamagnetism in free elements.
(*c*) Diamagnetism in unsaturated compounds.

In each case only elements are considered which fall outside the rectangle in Bohr's form of the periodic table (Fig. 1).

(*a*) *Diamagnetism in Saturated Compounds.*—The electronic theory of chemical combination affords a ready explanation of the fact that saturated compounds of diamagnetic elements are diamagnetic, and that their susceptibility follows the additive law.

It is well known that some elements are electropositive, *i.e.*, they tend to lose electrons to form positive ions; others are electronegative, *i.e.*, they tend to gain electrons to form negative ions. On the electronic theory of chemical combination, developed mainly by Kossel,[21] there is a transfer of electrons between the

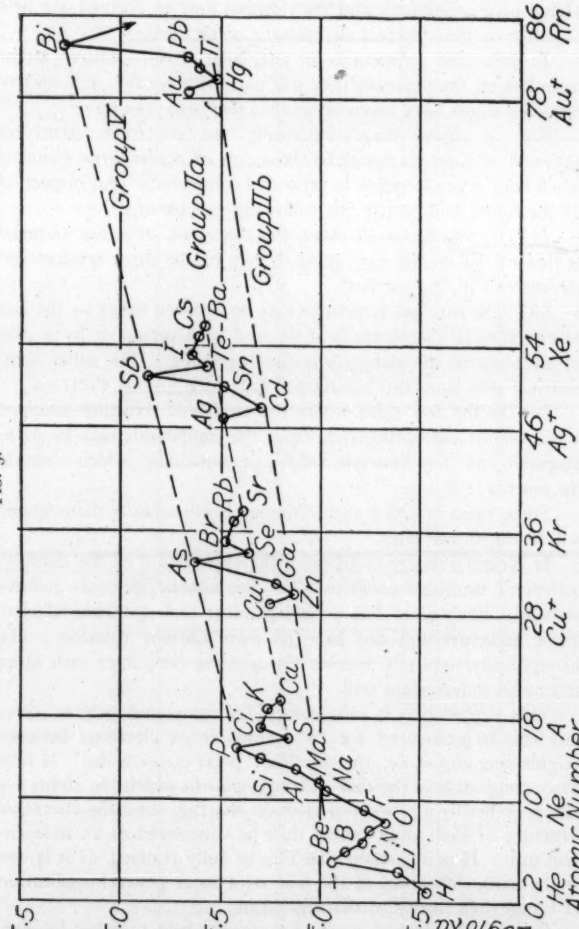


FIG. 3.

Relation between atomic susceptibility and atomic number for diamagnetic elements, according to Pascal.

atoms of a compound, and the charged ions so formed are held together by their mutual electrostatic attraction.

In saturated compounds in particular, electropositive atoms have lost all the electrons they will part with readily, and electronegative atoms have taken up all that they will take up.

Fig. 4 shows diagrammatically the electronic structures assumed on Kossel's theory by the atoms of diamagnetic elements when held in combination in saturated compounds. An inspection of the figure will justify the following conclusions.

(*a*) In practically all cases, the electronic structure assumed is that of one of the rare gases or one of the three symmetrical structures Cu^+, Ag^+ or Au^+.

(*b*) The rare gas structures may be attained either by the loss of electrons in the elements at the end of a period or by a gain of electrons in the elements at the beginning. The other symmetrical structures can be attained only by a loss of electrons.

(*c*) In the few cases where the electronic structure assumed is not one of the symmetrical ones, the compounds may be paramagnetic, as for example, cupric compounds, which contain the ion Cu^{++}.

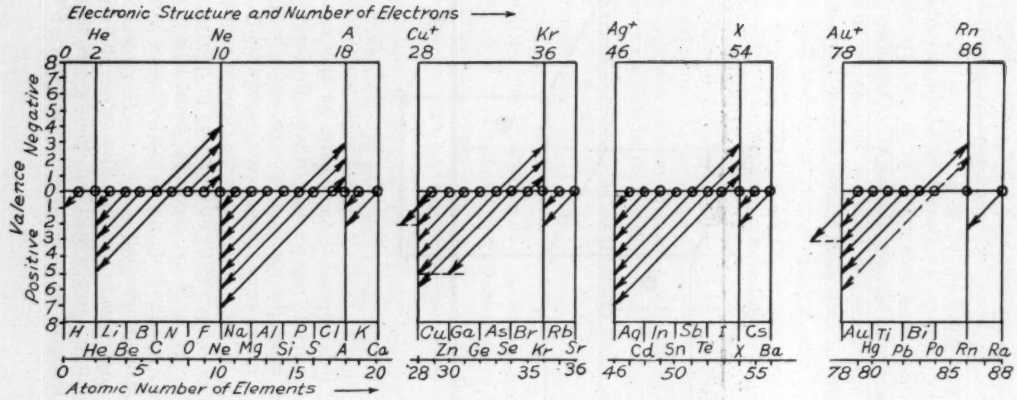
Some cases in which such compounds are actually diamagnetic will be mentioned later.

If Kossel's theory is adopted, the explanation of the diamagnetism of saturated compounds of diamagnetic elements follows at once. Each atom has an independent and symmetrical electronic structure and can have its own Larmor rotation. The susceptibility naturally follows the additive law, since each atom acts as an independent unit.

This explanation is satisfactory for compounds whose structure can be accounted for by a transfer of electrons between neighboring atoms, *i.e.*, the so-called "polar compounds." It falls down completely in the case of compounds in which the atoms are held together by a process of electron sharing, since the electronic structure of each atom cannot then be considered as an independent unit. It is important that this be fully realized, as it is one of the main difficulties in the way of a more general application of Langevin's theory of diamagnetism.

One of the simplest cases of molecules held together by electron sharing is that of the halogens. The molecules are diatomic

FIG. 4.



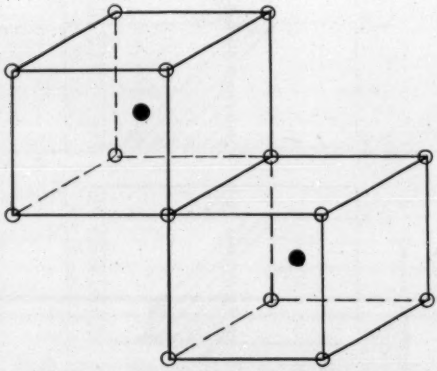
Electronic structure of atoms of diamagnetic elements in saturated compounds. (After Kossel.)

and the two atoms complete each other's outer electronic structure by sharing two electrons. On the Lewis-Langmuir theory, a Cl_2 molecule is represented as in Fig. 5.

On the Bohr theory, we must think of the shared electrons as describing orbits round both nuclei, or at any rate round a point placed symmetrically between the nuclei. On either theory there is so much interconnection between the electron structures that we cannot think of each atom having its own Larmor rotation.

In spite of this, it is an experimental fact that the suscepti-

FIG. 5.



Chlorine molecule according to the Lewis-Langmuir theory.

bility of Cl, Br and I is the same in the elemental form as in the compounds. It is impossible to account for this as the assumption that the molecule rotates as a whole; the large moment of inertia would make the rotation so slow as to be quite incompatible with the measured diamagnetic susceptibility. The only way out seems to be to assume that the electron structure of each atom can rotate independently in some way in spite of the electron sharing. This is hard to reconcile with either the Lewis-Langmuir theory or the Bohr theory, and we must look to further work to elucidate the question.

(*b*) *Diamagnetism in the Free Elements.*—In a large number of cases, the atomic susceptibility of diamagnetic elements is the same in the free state as in saturated compounds. The names of

the elements for which this has been proved experimentally have been printed in italics in Table VI.

Some attempts will now be made to connect the magnetism of diamagnetic elements in the free state with various other properties:

(*a*) The crystal structure as investigated by X-ray measurements.

(*b*) The electrical conductivity.

(*c*) The Hall effect.

(*d*) The magnetic behavior of single atoms, as investigated by Gerlach and Stern by the study of the deflection of streams of atoms in a non-uniform magnetic field.

(*e*) The dimensions of electron orbits as determined by calculation from optical and X-ray energy levels.

(*f*) The quantum numbers assigned in Pauli's scheme to the electron orbits of atoms in the normal state.

In the present state of our knowledge, such an attempt is bound to be very incomplete, especially in the later columns of the periodic table, where the crystal structure is more complicated and where a number of anomalies present themselves in the electrical conductivity, the Hall effect and the thermo-electric power. A close study, both experimental and theoretical, of these effects and their relation to magnetism, cannot fail to disclose interesting results.

Column I.

This comprises the alkalies, Li, Na, K, Rb and Cs (Group I*a*), and the metals Cu, Ag and Au (Group I*b*).

In the solid form these metals are characterized by (*a*) the strictly cubical form in which they crystallize, centred cubic for the alkalies, and face-centred cubic for the metals of Column I*b*; (*b*) their high conductivity for heat and electricity; (*c*) a Hall effect whose sign is that given by the ordinary theory and whose magnitude is in accordance with the existence of one conducting electron per atom.

The calculations of Hartree [17] on the dimensions of the orbits of the electrons in the Na and K atoms indicate definitely that the orbit of the valency electron is so large that the electron could not complete it without penetrating neighboring atoms. It is thus natural to think that it becomes the conducting electron. Whether it is truly "free" as the older theories of conduction required,

or whether it moves along a row of atoms, taking a loop round each according to the ideas of Höjendahl,[22] it is hard to say now, but there seems no doubt that there is but one conducting electron per atom, in accordance with the calculations based on the Hall effect.§

The calculations of Foote,[23] in agreement with those of Hartree for Na and K, show further that the same considerations apply to the other alkali metals. They could probably be extended to the metals of Group I*b*.

Bohr [24] has recently proved definitely that free electrons make no contribution to diamagnetism. The atomic susceptibility of these metals in the pure form should thus be that due to the electrically symmetrical core, that is, it should be the same in the metals as in the compounds.

Owing probably to the difficulty of obtaining these metals free from iron, this seems to have been satisfactorily verified only in the case of gold. For Ag and Cu, the atomic susceptibility in the metallic state is somewhat lower than those of Table VI, -19.4×10^{-6} and -5.7×10^{-6}, respectively. According to most measurements, the alkali metals actually seem to be paramagnetic. Miss Crow [15] has, however, recently obtained values for the atomic susceptibility of K, Rb and Cs, namely, -1.9×10^{-6}, -7.0×10^{-6} and -8.0×10^{-6}, which are of the right sign, although distinctly smaller than those of Table VI.

It seems important to decide whether the discrepancy is real or due to impurities. Work on this point is in progress at McGill University at the present time.||

Column II.

This includes the transition elements Be and Mg, the alkaline earth elements Ca, Sr, Ba and Ra (Group II*a*), and the metals of Group II*b*, Zn, Cd, and Hg.

§ Frenkel, who has recently given a new theory of Conduction in Metals (*Zs. f. Phys.*), comes to the same conclusion from general considerations of the energy in the solid state.

|| Mr. L. C. Jackson (*Nature*, 117, p. 449 (1926)) has taken the results of Miss Crow on the susceptibility of the metals K, Rb, and Cs, together with measurements on salts of these metals as a basis for the calculation of the contribution of the valency electrons to the susceptibility of the metals. A new measurement of the susceptibilities of the metals is important to decide whether the contribution is as calculated by Jackson, or whether it is nil in accordance with Bohr's calculation.

These elements fall into two classes from the point of view of crystal structure:

Hexagonal: Be, Mg, Zn, Cd, and probably Hg.

Face-centred Cubic: Ca.

No data seem to exist for Sr, Ba, Ra. It would be interesting to know whether they crystallize in the same way as Ca.

Susceptibility considerations divide the elements of this column into the very same sub-groups. In Fig. 3 Ca, Sr and Ba fall accurately on one straight line, Be, Mg, Zn, Cd and Hg on another. Perhaps it is best not to attach too much importance to the fact that Be fits in with other elements of its group from the point of view of susceptibility, as it is the only element of atomic number below 12 which does so, but it is very interesting that Mg should fall in with Group II*b* from this point of view as well as from that of crystal structure. Its chemical properties would place it rather with Group II*a*.

The Hall effect seems to give little useful information about electronic structure in this column as far as the present theory of the effect goes, as it is distinctly anomalous except for magnesium.

The atoms of these elements all possess a symmetrical core and two valency electrons. The assignment of quantum numbers to the valency electrons by Bohr indicates that they describe elliptic orbits of maximum eccentricity represented on Pauli's scheme by $(n, 1, 1)$. In a magnetic field, these electrons will assume magnetic quantum numbers $\pm\frac{1}{2}$. Hence we may expect the atoms to be diamagnetic both when they have their valency electrons, and when these are stripped off.

It is rather difficult to decide what is the probable state of the valency electrons in the elements in this group in the metallic state.¶ The calculations of Hartree for ionized Ca indicate that their maximum distance from the nucleus is 2.12 A., whereas the atomic radius obtained for Ca from crystal data is 1.96 A. Since the orbit is neutral Ca will be slightly larger, there is no room for the full orbits in the sphere occupied by the atom, unless their dimensions are considerably diminished, due to the mutual repulsion of electrons in adjoining atoms. On the whole, it seems

¶ Frenkel (see note above) comes to the conclusion that the valency electrons in these atoms probably describe a small number of orbits round a nucleus before passing to the next one.

probable that the valency electrons are " free." The fact that the conductivity is notably lower than in the metals of Column I, in spite of the presence of two conducting electrons per atom instead of one, must be ascribed to a diminution in the mean free path, not incompatible with the notable diminution in atomic volume.

The experiments of Gerlach and Stern on Zn, Cd and Hg indicate definitely that these atoms are non-magnetic in the isolated state.

Column III.

This includes the metals B, Al, in Group III*a*, and Ga, In, Tl in Group III*b*.

The only one of these elements whose crystal structure is at all well known is Al, which crystallizes as a face-centred cube. Of the three valency electrons, two according to Bohr are in (3, 1, 1) orbits (Pauli's notation) and one in a (3, 2, 1) orbit. The latter being most lightly bound is probably the conducting electron which is fairly free, as the high conductivity indicates. The neon-like core and the other two electrons will have no resulting magnetic moment, according to Pauli's theory, since the latter have magnetic quantum numbers $\pm\frac{1}{2}$ in a field. We may thus expect Al to be diamagnetic, in contradiction to Honda's measurements ($K_m = +0.65 \times 10^{-6}$). The discrepancy seems easily explained by the fact that iron is a common impurity in Al.**

Of the other elements in the column, Be, Ga, Tl, according to Pascal, have a diamagnetic susceptibility in the pure form equal to that in the compounds, in agreement with the above considerations for Al.

Only one element of this column, Tl, has been studied in the atomic form by the Gerlach and Stern method. It was found slightly magnetic as one would expect from its having only one (6, 2, 1) electron.

Column IV.

This includes C and Si in Group IV*a* and Ge, Sn, Pb in Group IV*b*.

The crystal structure in this group is generally the tetrahedral structure of the diamond. This applies to C (diamond), Si, Ge, Sn (gray tin). Carbon and tin also form crystals of different

** Aluminum leaves used by the writer in alpha-particle experiments contained 0.15 per cent. of iron. E. S. B., *Proc. Roy. Soc.*, **A**, 105, p. 437 (1924).

types (graphite and white tin, respectively), whose structure does not seem to have been quite definitely determined. Lead is face-centred cubic.

According to Stoner's assignment of quantum numbers, the four valency electrons are in (n, 1, 1) and (n, 2, 1) orbits (Pauli's notation). In a magnetic field, the fourth quantum number m, will take up values $\pm\frac{1}{2}$, $\pm\frac{1}{2}$, so that there is no resultant magnetic moment, and the substances may be expected to be diamagnetic.

This is actually the case for C and Sn, whose susceptibilities have been measured in the pure form and found to be the same as in the compounds.

In the atomic form Sn and Pb are non-magnetic according to the experiments of Gerlach and Stern.[25] They observed no deflection of a stream of these atoms in a non-uniform magnetic field.

Column V.

This comprises N, P, As, Sb and Bi, all in Group V*b*.

These elements are all at the peaks of the curve of diamagnetic susceptibilities (Fig. 3).

The later members are also characterized by a large thermo-electric effect and a large Hall effect.

The very large diamagnetic susceptibility of the elements of this group is not easy to understand. Antimony has about twice, and bismuth about four times the susceptibility of their immediate neighbors.

In the case of the compounds, a rather larger susceptibility might be expected for these metals since they are the first of their respective period which tend to complete their outer electron shell of eight, instead of handing over their five valency electrons to neighboring atoms. (Fig. 4.) But it is hard to see how even this would lead to such large values of the atomic susceptibility, and still more difficult to explain the large susceptibility in the free state, where no electrons are available to complete the octet.

The crystal structure, worked out by James and Tunstall,[26] indicates a large amount of interaction of one atom with some of its neighbors. No doubt this plays a part in the rather striking magnetic and thermo-electric behavior of this group.

Column VI.

This comprises O, S, Se, Te, Po, all in Group VI*b*.

Here crystal measurements are entirely lacking except for some work of W. H. Bragg [27] on sulphur, which does not seem to be entirely conclusive. The paramagnetism of O as O_2 seems to be characteristic of the molecular structure. In S, Se, Te, the diamagnetism has been found to be the same in the elements as in the compounds.

Column VII.

This comprises the halogens, F, Cl, Br and I.

In all cases, except that of F, the atomic susceptibility is the same in the elements as in the compounds. This is very remarkable, since the compounds presumably contain these elements as ions with an electrically symmetrical structure, whereas, in the free state, these elements exist as diatomic molecules held together by a covalent bond, *i.e.*, by the sharing of two electrons. The difficulty of accounting for the diamagnetism of such a structure has already been emphasized.

Column VIII.

The case of the inert gases, He, Ne, A, Kr, Xe and Rn has already been considered in Section IV.

This closes the list of diamagnetic elements. The diamagnetic compounds of paramagnetic elements will be dealt with in the next section.

(*c*) *Unsaturated Compounds.*—The general case of unsaturated compounds is rather too complicated, and the measurements too few to warrant a lengthy discussion.

There are two types of unsaturated compounds: (*a*) Those in which two atoms of an even valency, or two atoms of an odd valency are associated.

Such a case occurs for instance in the compounds of Sn or Pb, in which these metals are divalent. If we take the oxides, for definiteness, two electrons belonging to the metal atom go to complete the electronic structure of the O atom. The metal atom retains two electrons in addition to the symmetrical electronic structure which forms its core. On Pauli's scheme these will be in (n, 1, 1) orbits, and will have magnetic quantum numbers $\pm\frac{1}{2}$ associated with them. Thus, the oxides of divalent tin or lead will naturally be diamagnetic, as experiment shows to be the case.

(*b*) The second class of unsaturated compounds comprises

such a compound as NO, in which an element of odd valency combines with one of even valency.

In such a case there is no possibility of a magnetic balancing of the electron orbits according to the Pauli theory. The compounds may thus be expected to be paramagnetic. Experiment shows that it is so in the case of NO.[28]

VII. DIAMAGNETISM IN THE PARAMAGNETIC ELEMENTS.

It has long been known that compounds of the elements included in the rectangles of Fig. 1, those which we have called *paramagnetic elements*, occasionally show diamagnetic quality. Some recent work has thrown a great deal of light on this apparent anomaly, especially in the case of the elements of Group VIII*b*, Fe(26), Co(27), Ni(28), Ru(44), Rh(45), Pd(46), Os(76), Ir(77), Pt(78).

Early in 1925, Ingersoll[29] announced that he had obtained non-magnetic nickel by cathode-ray sputtering. An interesting explanation of this was very soon put forward by Oseen,[30] which seems to have given the key to the solution of the problem in other cases also.

Oseen supposes that this non-magnetic nickel consists of atoms with the perfectly symmetrical electron structure of the Cu^+ ion, consisting of 2 K electrons, 8 L electrons, and 18 M electrons. Such Ni atoms would be separate symmetrical electrical units, presumably held together by some sort of residual attraction. The facts that the usual magnetic properties of nickel appear on heating the film and that the X-ray diffraction patterns, almost completely absent in the original film, also come out on heating, seem to strengthen this hypothesis.

Against this is to be set the observations of Gerlach and Stern[25] that the deflection of a stream of nickel atoms in a non-uniform magnetic field discloses very marked magnetic properties in the single atom.

But whether Oseen's theory is to be accepted to explain Ingersoll's non-magnetic film of nickel or not, it has opened the way to a theory of the diamagnetic quality of certain salts of paramagnetic elements.

The main part of the credit for this is due to Welo and Baudisch.[31] They carried out accurate determinations of the susceptibility of specially prepared samples of complex salts con-

taining iron and found a number of them diamagnetic. In their latest letter to *Nature*, they put forward the hypothesis that the diamagnetism of these salts is due to the fact that the atoms of paramagnetic elements have gained a sufficient number of electrons from neighboring atoms by sharing and transfer to attain the electronic configuration of a rare gas. They apply the ideas of Sidgwick [32] to determine the number of electrons shared or transferred by the various ions or molecules which may be attached to the metallic atom. In this way they show that a scheme of electron sharing and transfer based entirely on chemical evidence will give a perfectly satisfactory explanation of the observed magnetic properties of the compounds.

One example will suffice to indicate the principles involved. Potassium ferrocyanide, $K_4Fe(CN)_6$, has long been known to be diamagnetic. Now each univalent atom of K will contribute one electron to the iron atom by transfer. Each CN group will add one electron by sharing. The electronic structure of the iron atom, originally with 26 electrons, thus gains 10 to assume the structure of the rare gas krypton with 36 electrons.

Co and Ni are also shown to assume the electronic structure of Kr in the diamagnetic compounds which they form. In the same way, the metals of the next two triads assume the electronic structure of the rare gases Xe(54) and Rn(86) in those of their complex salts which Rosenbohm [33] has shown to be diamagnetic.

Welo and Baudisch extend their theory to explain the paramagnetic quality of certain other complex salts. This development is, however, beyond the scope of the present article.

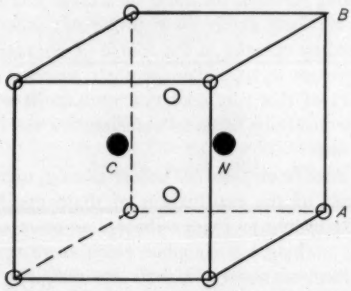
In connection with the application of the theory to diamagnetic complex salts, *e.g.*, those in which the electronic system of the central atom (Fe, Co, Ni, or any of the members of the other two triads) is made up to the full complement of a rare gas, one remark might be made.

Sidgwick has explained the structure of these salts from the point of view of the Bohr atom. Lowry [34] has applied to them the ideas of Lewis and Langmuir. Since the theory of diamagnetism applies equally to both, and since the second lends itself better to considerations of a chemical nature, we shall use the language of that theory. Taking again the case of potassium

ferrocyanide, we have to distinguish between the modes of binding of the K atom and the CN radicle to the central Fe atom. The K atom has positive electrovalency 1, and is ready to transfer its valence electron to the central atom. According to the Lewis-Langmuir theory, however, the structure of the CN radicle is as in Fig. 6.

The C and N atoms form a single cube, one of whose corners *B*, is without an electron. Such a system can only complete its octet, and at the same time contribute an electron to the central system, by a process of electron sharing. *B* becomes filled with an electron from the central system and *A* and *B* are shared by the CN radicle on the one hand, the Fe atom on the other hand.

FIG. 6.



The CN radicle according to the Lewis-Langmuir theory. (Only the L electrons are shown, four belonging to carbon, five to nitrogen.)

The same difficulty occurs in this case as in that of the Cl_2 molecule. The two systems, holding two electrons in common, are not independent, and it is very hard to see how each can have its own Larmor rotation. Since such complex salts are diamagnetic, however, and since their susceptibility can be obtained from that of the component atoms within the experimental error, as Welo and Baudisch have shown, the natural conclusion seems to be that there is much less interconnection between the electronic systems held together by electron sharing than appears at first glance from a consideration of the Lewis-Langmuir theory, and that each atom has its own Larmor rotation. More numerous and

more accurate data on the susceptibility of pure complex salts of paramagnetic elements cannot fail to throw light on this important question.

VIII. CONCLUSION.

It is not without some misgivings that this article is being sent forward for publication. The work of Stoner and of Pauli on the grouping of electrons within the atom has given such an impulse to the subject of atomic physics with special reference to spectroscopy and magnetism that it is almost impossible to keep abreast with the times, and a summary of recent work is out of date before it reaches the press. In addition, the writer feels that in this article he is contributing very little which has any claim to originality. Some of the ideas put forward here are doubtless running through the mind of a large number of physicists who are thinking about these problems; others the writer may have picked up casually in the course of his reading, without being able at present to trace them to their source. But the fact that a summary of this sort does not seem to have appeared in English may probably be taken as sufficient excuse for the publication of this one.

One point must be emphasized before closing, namely, the very formal character of the explanation of diamagnetism which is given here. According to Pauli's theory, an atom or atomic ion which contains nothing but complete electron groups is diamagnetic, but we have no conception how the magnetic moments of the several electrons composing a group cancel one another. We may say that the two electrons in the helium atom have equal and opposite magnetic quantum numbers, and therefore no resultant magnetic moment, but the model of the helium atom which satisfies this condition, and gives at the same time the proper energy levels, is yet to be proposed.

Perhaps we have reached here a point which we must not try to explain in terms of the laws of electrodynamics which obtain in the large scale world in which we live. Max Born, in his new book, "Problems of Atomic Dynamics," warns us of the possibility that the laws which hold inside the atom are different from those which we observe as holding on a larger scale. As to that, the future only will decide.

In conclusion the writer wishes to thank Dr. E. C. Stoner,

whose paper, "The Distribution of Electrons among Atomic Levels," first drew the writer's attention to the importance and interest of this phase of atomic physics, and with whom the writer has been in correspondence ever since.

To Dr. A. S. Eve, Director of this building, the writer is deeply grateful for his continued and stimulating interest.

REFERENCES.

[1] LANDOLT and BÖRNSTEIN: "Phys. Chem. Tables," 5th Ed., p. 1241.
[2] CABRERA: *Jour. de Phys.*, **6**, pp. 241, 273 (1925).
[3] LANGEVIN: *Ann. der Phys.*, 8th ser., **5**, p. 70 (1905).
[4] STONER: *Phil. Mag.*, **48**, p. 719 (1924).
[5] PAULI: *Zeits. f. Phys.*, **31**, p. 765 (1925).
[6] BOHR: "The Theory of Spectra and Atomic Constitution," Cambridge University Press (1922).
[7] HUND: *Zeits. f. Phys.*, **33**, pp. 345, 855; **34**, p. 296 (1925).
[8] PAULI: *Zeits. f. Phys.*, **2**, p. 201 (1920).
[9] TÄNZLER: *Ann. der Phys.*, **24**, p. 931 (1907).
[10] TAKÉ SONÉ: *Phil. Mag.*, **39**, p. 305 (1920).
[11] HECTOR: *Phys. Rev.*, **24**, p. 418 (1924).
[12] WILLS and HECTOR: *Phys. Rev.*, **23**, p. 209 (1924).
[13] JOOS: *Zeits. f. Phys.*, **19**, p. 347 (1923); **32**, p. 835 (1925).
[14] KOENIGSBERGER: *Wied. Ann.*, **66**, p. 698 (1898); *Ann. der Phys.*, **6**, p. 506 (1901).
[15] CROW: *Proc. Roy. Soc. Can.*, **19**, sect. 3, p. 63 (1925).
[16] BRAGG, JAMES, and BOSANQUET: *Phil. Mag.*, **44**, p. 433 (1922).
[17] HARTREE: *Proc. Camb. Phil. Soc.*, **21**, p. 625 (1923).
[18] PASCAL: *Ann. de Phys. et de Chim.*, 8th series, **16**, p. 531; **19**, p. 5 (1910); **25**, p. 289 (1912); *Comptes Rendus*, **158**, pp. 37, 1895 (1914); **159**, p. 429 (1914); **173**, p. 145 (1921); **173**, p. 712 (1921); **174**, pp. 457, 1698 (1922); **175**, pp. 814, 1063 (1922); **176**, p. 1887 (1923).
[19] HONDA: *Ann. der Phys.*, **32**, p. 1027 (1910).
[20] OWEN: *Ann. der Phys.*, **37**, p. 657 (1912).
[21] KOSSEL: *Ann. der Phys.*, **49**, p. 230 (1916).
[22] HÖJENDAHL: *Phil. Mag.*, **48**, p. 349 (1924).
[23] FOOTE: JOUR. FRANK. INST., **198**, pp. 344, 517 (1924).
[24] See National Research Council Monograph, "Theories of Magnetism," p. 103.
[25] GERLACH: *Phys. Zeits.*, **26**, p. 816 (1925).
[26] JAMES and TUNSTALL: *Phil. Mag.*, **40**, p. 233 (1920); **42**, p. 193 (1921).
[27] BRAGG, W. H.: *Proc. Roy. Soc.*, **A, 89**, p. 575 (1914).
[28] QUINCKE: *Wied. Ann.*, **24**, p. 347 (1885); **34**, p. 401 (1888).
[29] INGERSOLL: *Phys. Rev.*, **25**, p. 114 (1925).
[30] OSEEN: *Zeits. f. Phys.*, **32**, p. 940 (1925).
[31] WELO and BAUDISCH: *Nature*, **116**, pp. 359, 606 (1925).

[33] SIDGWICK: *Jour. Chem. Soc.*, Trans., **123**, p. 725 (1923).
[34] ROSENBOHM: *Zeits. f. Phys. Chem.*, **93**, p. 693 (1919).
[34] LOWRY: *Chem. and Ind.*, **42**, p. 316 (1923).

See also the following books:

Hall Effect: "Galvanomagnetic and Thermomagnetic Phenomena," L. L. CAMPBELL, Longmans, Green and Company, London (1923).

Crystal Structure: "X-rays and Crystal Structure," W. H. and W. L. BRAGG, Bell, London (1923).

"The Structure of Crystals," WYCKOFF, Chemical Catalogue Co., New York (1924).

Bibliography of the Hering Paracelsus Library.—A Souvenir of the Sesqui-Centennial, issued by the Hahnemann Medical College and Hospital of Philadelphia (1926, 32 pages), contains a complete catalogue, covering eleven pages, of the Paracelsus Library which was collected by the late Dr. Constantine Hering, a founder and a former dean of the college, and is now the property of the college. The library contains original treatises, translations, and commentaries by and about Philippus Theophrastus Bombastus of Hohenheim, called Paracelsus, who lived from 1493 to 1541 and was eminent as a physician and as a chemist. Many of the texts date from the sixteenth century. J. S. H.

Commercial Furfural.—D. H. KILLEFFER (*Ind. and Eng. Chem.*, 1926, **18**, 1217–1219) describes the manufacture of furfural from oat hulls, a by-product of the rolled oat industry. The oat hulls are ground, moistened with 5 per cent. sulphuric acid, and then treated with steam at a pressure of 60 pounds per square inch. The hulls contain from 32 to 36 per cent. of pentosans; these undergo hydrolysis, and the resulting pentose is then converted into furfural. Live steam is passed through the digester, maintaining the pressure stated. The steam and furfural, which pass from the digester, are conducted through a settling tank, then into a fractionating column. The furfural is collected, and is dried at a temperature not above 160° C. without vacuum distillation. The product is between 98 and 99 per cent. pure. Three digesters may be operated by two men. Three shifts, each working for six to eight hours, produce about 5000 pounds of furfural daily. The yield of furfural is in excess of 10 per cent. of the weight of the oat hulls used.

Prior to 1922 furfural could be obtained with difficulty, and the price ranged between $6.50 and $30 per pound. To-day it may be obtained in lots of 25 or 30 tons at 15 cents per pound.

Furfural is used in the manufacture of synthetic resins, as a germicide and fungicide in tree surgery, as a flavor in tobacco, as a solvent in shoe dyes and leather dressings, as a fly-repellant, and in the synthesis of numerous organic compounds. J. S. H.

LOW-PRESSURE ELECTRIC DISCHARGE IN INTENSE ELECTRIC FIELDS.

BY

C. DEL ROSARIO.

Research Assistant, Bartol Research Foundation; Junior Sterling Fellow, Yale University.

INTRODUCTION.

BARTOL RESEARCH FOUNDATION Communication No. 9.

SEVERAL investigations have been made on the emission of electrons by metals in intense electric fields; among these may be mentioned the experiments of Lilienfeld,[1] Millikan and Eyring,[2] and Gossling.[3] Schottky,[4] from theoretical considerations, calculated the field intensity required to pull out electrons from a metal surface and concluded that it is of the order of 10^8 volts/cm. The fields actually used in the experiments, however, were only 10^{-3} to 10^{-2} of this value. Millikan and Eyring advanced as a probable explanation for the difference the geometrical roughness or some chemical impurity on the metal surface. The importance of this phenomenon warrants further research. This present work was undertaken to find out, among other things, the effect on the electron emission of the residual gases and the applied potential difference as distinct from the field intensity.

EXPERIMENTAL METHODS.

The apparatus was designed with the idea of securing the most perfect conditions of shielding against stray currents and even electrostatic effects. The principle used for obtaining high electric fields was that involving the use of a fine fibre as the inner member of a cylindrical condenser, a difference of potential being maintained between the fibre and the outer cylinder.

For concentric cylinders the charge Q per unit length of the inner cylinder is given by the expression

$$Q = \frac{V}{2 \log_e b/a},$$

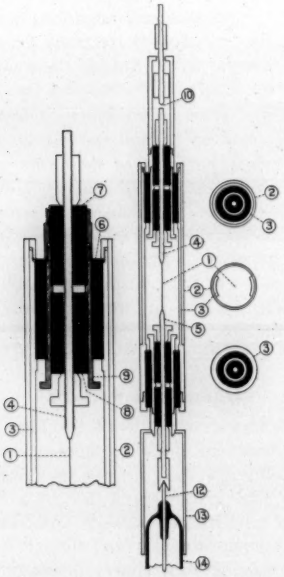
[1] *Phys. Ber.*, **2**, p. 1350 (1921); *Phys. Zeit.*, **23**, p. 506 (1922).
[2] *Phys. Rev.*, **27**, p. 51 (1926).
[3] *Phil. Mag.*, **1**, p. 606 (1926).
[4] *Zeit. f. Phys.*, **14**, p. 80 (1923).

where V is the potential difference between the cylinders; a, the radius of the inner cylinder and b, the internal radius of the outer cylinder. The field F at the surface of the fibre is

$$F = \frac{2Q}{a} = \frac{V}{a \log_e b/a}. \qquad (1)$$

In the experiments here described fibres of diameters smaller than those used by former investigators were used, so that equally

FIG. 1.



high fields were obtainable with lower values of V. By the use of fibres of different diameters, moreover, it was possible to obtain the same field with different values of V and so dissect out the significance of the fields and potential differences in relation to their influence on the production of electron current.

The main apparatus consists of a fine filament (1) (Fig. 1) of platinum or platinum sputtered quartz fibre, fixed in the axis

of two nickel cylinders (2) and (3), the former slipping over the latter. The inner cylinder was cut out laterally, leaving a skeleton as shown by the middle cross-section, thus facilitating the insertion of a new filament. The filament is held in the axis of the cylinder by small threaded rods (4) and (5), which can be moved up and down by small nuts to adjust the tension of the filament. Accurate centring and tension adjustment of the filament are necessary to prevent the breaking of the fine filaments which ranged from 5×10^{-4} to 10×10^{-4} cm. in diameter. The way in which the inner cylinder (3), the glass insulators (6), (7) and (8), the guard ring (9) and the filament holder (4) are rigidly interlocked can be easily seen in the enlarged section. The flange on the inner end of the guard ring shields the filament from the inductive effect from any changing dielectric soakage or any slight variable surface leakage across the insulator (6). At the upper end of the upper filament holder and shielded by an extension of the guard ring is a make-and-break contact (10) operated by a solenoid around an iron armature (11) (Fig. 2). The contact is made when testing whether or not the filament is broken. The lower end of the lower filament holder rests on a tungsten lead (12) (Fig. 1). This is partly shielded by a cylinder (13) held up by a helical spring. Further shielding when an electrometer is used may be obtained by the insertion of another cylinder inside the inner glass tube (14).

The experimental tube may be taken out from the pyrex glass container in the following simple way. The top of the container is blown out and the chain (18) is unhooked from the armature (11); then the tube is taken out by parts—first the tube holder (19), then the outer cylinder (2) and then the rest of the tube together.

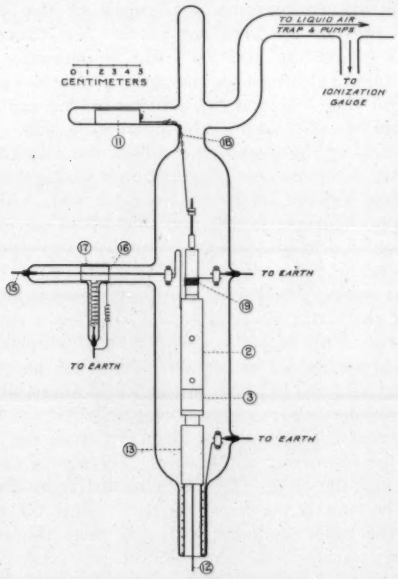
The positive terminal of a high potential storage battery was connected across a megohm resistance to the cylinder through the tungsten lead (15). The grounded[5] thin copper cylinder (16) fused to the inner wall of the glass tube, and the lead foil (17) wrapped around this tube prevented any leakage along the glass from the cylinder lead (15) to the filament lead (12). The latter was connected to a sensitive galvanometer through a 10^5 ohm resistance. The potential difference between the cylinder and

[5] The terms "grounded" and "earthed" are here used in the sense of connection to a common point. The connection of that point to earth is of course immaterial.

the filament was measured by a static voltmeter and this value was checked up by the sum of the current voltmeter readings for sections of the storage battery.

The experimental tube container was connected to the same vacuum system as was used in a previous investigation.[6] The

FIG. 2.



tube leading to the hydrogen supply employed in that investigation was, however, cut off. The pressure of the residual gas was measured by an ionization gauge of the type used by Dushman and Pfund.[7] The pressure as recorded by such a gauge is given by an expression of the form

$$p = c\frac{i}{I}$$

where I is the electron current, i the ionization current and c

[6] *Phys. Rev.*, **28**, p. 709 (1926).
[7] *Phys. Rev.*, **17**, p. 7 (1921).

the gauge constant. It is known that c is reproducible with reasonable certainty in gauges of approximately the same dimensions. This type of gauge has been used at the Bartol Foundation and at Yale University for some time and different measurements by different observers have confirmed the value $c = 0.23$ for air. For mercury vapor the value of c is 0.04.

The experimental tube, the ionization gauge and the liquid-air trap were baked in an electric furnace at 770° K. for eight hours with the pumps going continuously. The ionization gauge was further outgassed by electron bombardment. Great care was taken against grease contamination on the experimental tube before it was put inside its glass container, and gloves were always used in handling all the parts. The pressure of the residual gases was of the order of 10^{-8} mm. Hg in those experiments where the highest vacuum was used.

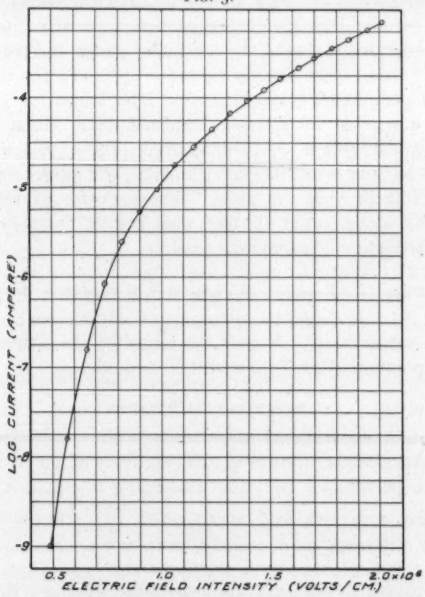
Fig. 1 is drawn to scale. Although the case is not one of infinitely long concentric cylinders, it is a fact that the calculated value of the field found by equation (1) should give a reasonably accurate value for points near the centre of the filament. It is at these points that the field would be a maximum.

EXPERIMENTAL RESULTS.

The first experiments were made with a platinized quartz fibre whose diameter measured to an accuracy of 10 per cent. with a microscope was 5×10^{-4} cm. According to equation (1), this would give a surface field of 1.1×10^{6} $\frac{\text{volts}}{\text{cm.}}$ for the maximum potential difference used, namely, 2080 volts. No electron current for this field intensity could be detected with a galvanometer with sensitivity of 2×10^{-10} amp. per scale division. Beyond this value of the field the sputtered platinum was torn off from the quartz fibre. With platinum filaments 5×10^{-4} cm. in diameter, however, the field was raised to 2.0×10^{6} $\frac{\text{volts}}{\text{cm.}}$ corresponding to the maximum potential difference obtainable with the storage battery—4000 volts; still no electron current of measurable magnitude (0.2 of a scale division) was observed. However, when a small quantity of air—of the order of 10^{-4} mm. Hg—was admitted into the experimental tube, it was possible to obtain consistent and reproducible current, and to secure field intensity curves which are very similar to those obtained by Millikan and

Eyring. A sample of these curves is shown in Fig. 3. A coarser filament, 10×10^{-4} cm. in diameter, was used with approximately the same gas pressure in the tube, and it was observed that the current could first be detected at about the

FIG. 3.



same potential difference and not at the same field intensity as that used with the finer filaments.

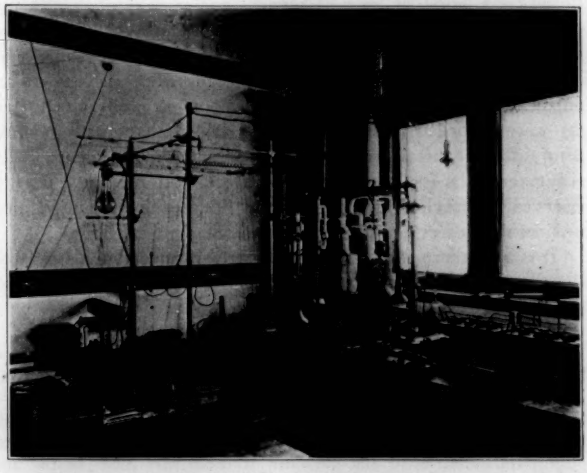
The apparatus was first set up in the Bartol Research Foundation Laboratory of The Franklin Institute. An identical arrangement, subsequently set up in the Sloane Laboratory, gave completely confirmatory results.

DISCUSSION OF RESULTS.

The above experimental results cast doubt on the conclusion of previous observers that the current they obtained was due to the pulling of electrons off from the metal surface by the electric

field. Using Millikan's data for tungsten, the electron current which corresponds to half of the maximum field intensity used in these experiments would be of the order of a million times that which could produce a galvanometer deflection of one scale division. It is of course possible, although improbable, that electrons may be pulled off very much easier from tungsten than from platinum. Of course, in the writer's experiment, although

FIG. 4.



the fields at the surface of the wires were as high as those used by Millikan and Eyring, the actual potential differences were less, on account of the fineness of the wires used. It is conceivable that had the writer gone to the same potential differences as those used by Millikan and Eyring, currents of the order of magnitude of those obtained by them might have resulted. In this connection it is a significant fact that, in the writer's experiments with gas present and with different sized wires the potential difference rather than the field was the quantity which determined the point at which observable currents were obtained. It is, moreover, difficult to avoid the significance of the similarity between Millikan's and Eyring's log-current-potential curves and those

obtained by the writer when gas was the known cause of their origin, particularly in view of the fact that the writer's experiment gave no measurable current when the vacuum as recorded by his ionization gauge was of the order 10^{-8} mm. mercury. Presumably, if the currents were due to gas, and were determined by potential difference rather than by the field at the surface of the wire, the vacuum conditions occurring in Millikan's and Eyring's experiment were more stringent than those necessary in the writer's work, at least as regards comparison of results for corresponding fields. Vapors in small amounts would not have been recorded on the McLeod gauge used in Millikan's and Eyring's experiments, while in the present work the use of an ionization gauge insured that grease vapors as well as ordinary gas were recorded, if present. It is hoped that further work using different metals, modified electrodes and more intense fields will give basis for more definite explanation for the currents observed by previous investigators working with field intensities considerably lower than those used in these experiments.

It is a pleasure for the writer to here acknowledge his indebtedness and express his thanks to Professor Swann, under whose direction this work was done.

The Proportions of Krypton and Xenon Contained in Air. C. MOUREU and A. LEPAPE. (*Comptes Rendus*, July 19, 1926.)—Ramsay and Travers shortly after their discovery of krypton and xenon in the residue left after the evaporation of liquid air made a rough determination of the amounts of these rare gases in the air and found that by volume air contains .000001 of krypton and .00000005 of xenon. A second determination made by Ramsay a few years later gave proportions for both gases much smaller than the first results. The authors of this paper use a spectrophotometric method and obtain the following proportions for the five rare gases of the atmosphere:

	By Weight.	By Volume.
Argon	.0129	.009323
Neon	.000012	.000018
Helium	.0000007	.000005
Krypton	.000003	.000001
Xenon	.0000004	.00000009

G. F. S.

DIELECTRIC CONSTANT OF BROMINE.

PART II.

BY

ARTHUR BRAMLEY, Ph.D.,

Bartol Research Fellow.

ABSTRACT.

BARTOL RESEARCH FOUNDATION Communication No. 10.

USING an electrostatic method, a study was made of the variation of the dielectric constant ε of bromine vapor with pressure, temperature and electric intensity. The curves obtained by plotting $\varepsilon - 1$ against pressure for constant temperature and potential gradient are concave upwards at 23.9° C., rectilinear at 28.5° C. and concave downwards at 80° C. (Fig. 2). Since the values of the dielectric constant obtained at 23.9° C. were measured by a high-frequency method (JOUR. FRANK. INST., June, 1926) no data on the dependence of the dielectric constant with electric field were obtained but for the two higher temperatures taken by the electrometer method, the effect of the potential gradient on the dielectric constant was observed. For the linear curve taken at 28.5° C. no effect was obtained by changing the field from 58 volts to 285 volts, but for those measured at 80° C. app., a considerable variation was observed which depended on the pressure of the vapor. This dependence of dielectric constant with electric field gives a good account of the effects noticed by Wolf (*Phys. Zeit.*, **27**, 1926) where the dielectric constant of water vapor and ammonia were found to depend on the distance apart of the condenser plates for the same capacity and frequency, the method used being a heterodyne beat method. Values of the dielectric constant measured for a mixture of air and bromine vapor give results which confirm the additive law.

If we regard the band spectrum of a diatomic gas as due to the rotational and vibrational energies of the two ions composing the molecule, then the electric moment of the molecule ought to depend on the vibrational energy of the ions, *i.e.*, on their average distance apart. Since the probability of the molecule being in any one vibrational state of energy e_n is proportional to

$$e^{-\frac{e_n}{kT}},$$

the electric moment and, therefore, the dielectric constant ought to depend on the temperature through a factor of the form

$$\sum_{n=0}^{\infty} \alpha_n e^{\frac{e_n}{kT}}.$$

Applying the theory, developed from this viewpoint in the following discussion, to the case of the anomalous temperature variation of bromine and water vapor, we find that an accurate account of this temperature phenomenon can be obtained by taking for λ_0, the wave-length corresponding to e_0, the following values:

In the case of HOH

$$\lambda_0 = 3.0\mu,$$

which is in excellent agreement with the maximum absorption band of water vapor; in the case of Br_2 vapor

$$\lambda_0 = .9\mu.$$

In order to test the correctness of this value, a series of measurements was carried out on the absorption of Br_2 between .80μ and 2.0μ since no data were obtainable in this case. The data taken from these measurements show a broad absorption band in Br_2 vapor beginning at .95 and extending to 1.5, which confirms the theory in this respect (Fig. 3).

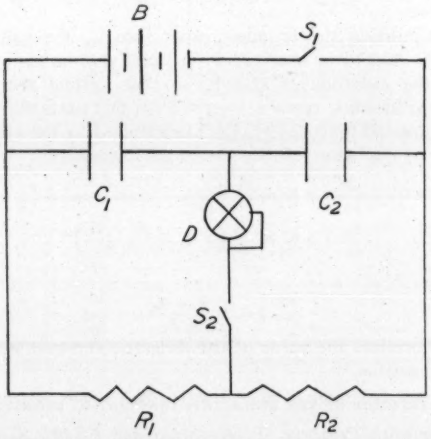
DESCRIPTION OF APPARATUS.

For the measurement of the variation of the dielectric constant with pressure, temperature and electric field, an electrometer method was employed, the diagrammatic sketch of the apparatus being shown in Fig. 1.

The electrometer system and connections consists of two condensers C_1 and C_2 in series with a battery B, whose voltage can be adjusted to various values and a key S_1 to open and close the circuit. The condenser C_1 is the same as that described in the previous paper on this subject (JOUR. FRANK. INST., July, 1926) and is used as the condenser for containing the bromine vapor whose dielectric constant is to be determined. The condenser C_2 is a standard air condenser of approximately the same capacity as C_1—100 cm.—and is used as the standard for comparison. One pair of the quadrants of the electrometer are connected to one set of plates of the condensers while the other pair of quadrants are connected through an electrometer key S_2.

to a potentiometer arrangement which allows the potential of this pair of quadrants to be accurately varied. The potentiometer consists of two high resistances R_1 and R_2—order of one megohm—placed in series with the battery B through the key S_1 and a connection from between these resistances to the electrometer key S_2. By changing the value of the resistances R_1 and R_2 the potential of the electrometer quadrants can be finely adjusted with respect to the battery B. In the experimental

FIG. 1.



arrangement used in this investigation, the resistances R_1 and R_2 could be changed by steps of 1 in 10^5 of the total resistance of R_1 and R_2. The electrometer D, condenser C_2 and key S_2 are contained in an earthed metal box while the electrical connections between the condenser C_1 and the electrometer system are run through metal tubes so that the circuit is completely shielded from external influences.

In the process of determining the change in capacity of C_1 with the bromine vapor under different conditions of pressure, etc., the keys S_1 and S_2 were first opened and the electrometer adjusted so that on closing S_2 no deflection of the needle was noticed. The resistances R_1 and R_2 were then adjusted to some definite value and the key S_1 closed, the deflection being noted.

The value of the ratio R_1 and R_2 was then changed until on repeating this procedure no deflection of the electrometer could be detected; at this particular value of R_1 and R_2 the potential of the two pairs of quadrants was the same, so that we have the result that

$$\frac{C_1}{C_2} = \frac{R_2}{R_1},$$

since the capacity of the electrometer system has no effect on the relation between the capacities and resistances when the circuit is balanced.

On admitting the bromine vapor into C_1 the value of the resistances had to be changed by a small amount $\triangle$ in order to balance the electrometer system, so that, calling the dielectric constant of bromine vapor ε, $\varepsilon = 1 + \delta$ for that particular pressure, temperature and potential gradient determined by the value of the potential of the battery B, we obtain the expression

$$\frac{C_1}{C_2}(1+\delta) = \frac{R_2 + \triangle}{R_1 - \triangle}$$

$$\frac{R_2}{R_1}(1+\delta) = \frac{R_2}{R_1}\left(1 + \triangle \frac{R_1 + R_2}{R_1 R_2}\right)$$

or

$$\delta = \triangle \frac{R_1 + R_2}{R_1 R_2}$$

which determines the value of the dielectric constant in terms of known quantities.

VARIATION OF THE DIELECTRIC CONSTANT OF BROMINE.

Vapor with Pressure, Temperature and Electric Gradient.—The bromine used in these experiments was purified by allowing it to stand for several days over P_2O_5 and then by introducing it into a vacuum system where it was frozen over liquid-air while air and other gases of lower boiling-point were pumped out. A given volume of this purified vapor at the pressure corresponding to its vapor pressure at room temperature was allowed to flow into the condenser system. This process was repeated until the bromine in the condenser C_1 reached the same vapor pressure as the vapor in equilibrium with the liquid. The dielectric constant was determined at each given step in the operation for room temperature and one higher temperature, a series of readings being taken at each of these steps for different field intensities. The electric gradient was changed in these experiments by changing

the value of the potential of the battery B—the values of the potential given in Table I are those of the battery from which the ratio of the potential gradient in C_1 can be immediately determined.

Résumé of the values of the dielectric constant ε obtained for various pressures, temperatures and potential gradients. The

TABLE I.

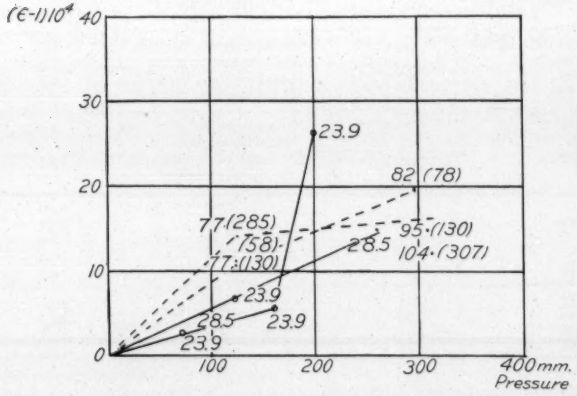
Pressure of Br_2 Vapor.	Temperature.	Potential Gradient of Battery.	$(\varepsilon-1)\ 10^{-4}$.
122 mm. of Hg.	23.9° C.	High-frequency method	6.7
160	23.9° C.	High-frequency method	5.2
200	23.9° C.	High-frequency method	26.2
72	23.9° C.	High-frequency method	2.7
100	28.5° C.	No measurable effect on changing potential	5.2
257	28.5° C.	No measurable effect on changing potential	14.7
126	77	285	14.0
		208	13.0
		58	11.0
		128	10.4
144	120	78	14.7
312	104	307	12.0
310	100	200	14.7
306	95	130	14.7
295	82	78	19.4

data given in this paper have not been referred to standard conditions.

A few typical examples of the type of curve obtained by plotting $\varepsilon - 1$ against pressure for different temperatures and electric fields have been plotted in Fig. 2. Examination of these curves shows that as the temperature is raised the character of the phenomena changes. The curves obtained at 23.9° C. by the high-frequency method have the same general outline as the curves obtained by Zahn for HOH (*Phys. Rev.*, March, 1926), the quantity $\varepsilon - 1$ increasing with pressure more rapidly than the first power. The linear curve for 28.5° C., which is independent of the electric gradient in the condenser, appears to behave in the normal manner that the classical theory of dielectric constants would predict except that the values of the quantity $\varepsilon - 1$ found experimentally are approximately twice the value predicted by calculation from the index of refraction. The curves obtained

at 77° C. are of the same general form as those found by Wolf (*Phys. Zeit.*, **27**, 1926) for NH_3, and have a decreasing tangent with increasing pressure, the reverse of the effect exhibited by the curve obtained at 23.9° C. It also exhibits the same phenomena with the same characteristic dependence of dielectric constant with electric gradient as that found by Wolf for NH_3 by varying the distance apart of the plates of the condenser keeping the capacity

FIG. 2.



In the above diagram the unbracketed numbers refer to temperatures, bracketed to voltages of the battery *B*.

and frequency for vacuum constant. The results obtained in this work indicate that this phenomenon is due to the dependence of the dielectric constant with potential gradient between the plates of the condenser.

THEORETICAL DISCUSSION.

The dielectric constant, calculated from the Lorentz relation for indices of refraction, is given by the equation

$$\frac{K-1}{K+2} = \alpha \sum_{s=1}^{\infty} \sum_{p=1}^{\infty} N_s A_{sp} \gamma_{sp} \lambda^3_{sp},$$

where A_{sp} is the probability of a transition from some particular state s to any other state p, such that the line with wave-length λ_{sp} is absorbed, the life of the electron in the state p being γ_{sp} and where the total number of atoms in the state s is N_s.

From the theory outlined in the first paper on this subject ("Dielectric Constant of Bromine," JOUR. FRANK. INST., July, 1926), we obtained a relation for γ_{sp} in terms of the temperature of the form

$$\gamma_{sp} = \frac{t_{sp} e^{-\frac{\varepsilon_s}{kT}}}{1 + \sigma_{sp} e^{-\frac{\varepsilon_p}{kT}}},$$

which becomes

$$\gamma_{sp} = \frac{t_{sp}}{\sigma_{sp}} e^{\frac{h\nu(sp)}{kT}},$$

provided

$$\sigma_{sp} > > 1$$

where t_{sp} and σ_{sp} are independent of the temperature T, so that we obtain finally for the relation between the dielectric constant and the temperature, the relation

$$\frac{K-1}{K+2} = \beta P \sum_{s=1}^{\infty} \sum_{p=1}^{\infty} A^{p}{}_{s} e^{\frac{h\nu(sp)}{kT}} \frac{t_{sp}}{\sigma_{sp}} \lambda^{2}{}_{sp}$$

where P is the pressure of the vapor.

At high temperatures, the factor $e^{\frac{h\nu(sp)}{kT}}$ can be replaced by unity since the temperature variation is extremely small, but as we lower the temperature continuously, one of the terms in the sequence

$$e^{\frac{h\nu(sp)}{kT}}$$

will tend to predominate over the sum of the remaining terms of the series. The term which shows this tendency most markedly will be that for which the value of $\nu(sp)$ is the greatest, other factors being equal, *i.e.*, it will be one of the first items of the sequence. Since it is evident that the frequency under discussion must refer to the absorption frequencies of the infra-red band spectrum of the molecule, we ought to find that a frequency corresponding to one of the head terms of the infra-red band system accounts for the anomalous temperature variation found in HOH and Br_2 vapor.

If we take for the wave-length λ, corresponding to the frequency ν appearing in these relations, the value

$$\lambda = 3.0\mu$$

in the case of water vapor, then an accurate account can be given of the change in the dielectric constant of water vapor with temperature (for data see Zahn, *Phys. Rev.*, June, 1925). The value of the wave-length given above corresponds to the maximum absorption at the head of the infra-red band spectrum (Coblentz, *Bull. of Bur.*, 7, 631, 1911).

In order to account for the temperature change in bromine vapor from 23.9° to 28.5° C., we have to take for the wave-length λ,

$$\lambda = .9\mu .$$

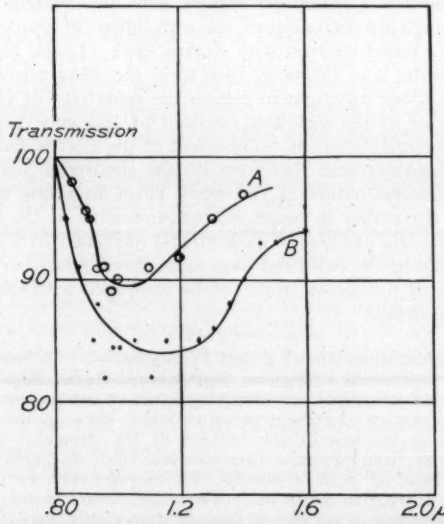
In order to test the correctness of this value, since no data were obtainable for the absorption of bromine in the near infra-red, a series of measurements was made on the absorption of bromine between .80 and 2.0μ; the data obtained from these measurements are given in Table II.

TABLE II.

Wave-length in μ.	% Transmission.			Average.
	With Bromine in Cell.			
.82	100	—	—	100
.86	94	94	86	91
.90	90	88	88	89
.94	91	85	87	88
.98	87	84	80	84
1.00	86	82	85	84
1.10	86	81	78	82
1.20	82	82	83	82
1.30	87	86	84	86
1.40	91	91	88	90
	Same Cell Filled with Air.			
.82	92	90		91
.86	100	95		98
.90	97	94		96
.94	90	92		91
.98	87	90		89
1.00	90	91		90
1.10	89	93		91
1.20	89	94		92
1.30	97	93		95
1.40	97	98		97

In the taking of a series of readings the accuracy of the readings depends on the fluctuation of the zero during the time required for taking the zero, the transmission through the cell, the transmission with the cell removed and the second zero. Since in the taking of the set of readings tabulated above, the zero never shifted more than one division and since the smallest difference

FIG. 3.



The curve *B* and the experimental points associated with it refer to the values of the transmission of a tube, 1m. long, filled with Br_2 vapor, while curve *A* and experimental points related to it, marked by o, give the data obtained with the same tube but free from Br_2 vapor.

used in the calculations of the transmission was 19 divisions, the error was never greater than 5.2 per cent., while the error for values of the wave-length greater than .90μ never exceeded 2.5 per cent. on account of the increased sensitivity of the instrument.

The graph of the average transmission against wave-length given in Fig. 3 shows a broad absorption band in bromine between .96 and 1.40μ, which is in good agreement with the band predicted from the data for the dielectric constant.

The taking of these measurements was made possible through

the courtesy of Professor Barnes, Bryn Mawr College, who placed at my disposal his infra-red spectroscope and assisted with the taking of the observations. Photographic measurements were also made of the absorption band which confirmed the readings taken by the thermopile method.

Returning now to a consideration of the effect of the electric field on the specific inductive capacity, we see that the variation of the dielectric constant of vapors with the electric gradient arises through the variation of the probability of transition and life of the excited electron with electric field. In the band spectrum of water and bromine, therefore, the head terms of the absorption spectrum ought to exhibit the same type of characteristic behavior as the dielectric constant of the same vapor does with the potential gradient. The effect of the electric field on the dielectric constant and, therefore, on the absorption band, is of the same general nature as the Stark effect in a line spectrum. So far as the author is aware, no measurements of the temperature and electric gradient (Stark effect) variation of absorption band spectra in the infra-red have been investigated, so that the predictions of the theory could not be compared with experiment in this one detail.

Paradichlorobenzene as a Soil Fumigant.—E. O. ESSIG (University of California, College of Agriculture, Agric. Exp. Station, *Bulletin 411*, 1926, 1–20) recommends the use of paradichlorobenzene for the destruction of certain parasites which prey on the roots of fruit trees, at or beneath the surface of the ground. The dose applied varies from ¾ ounce to a tree less than six years old to a maximum dose of 3 or 4 ounces; the average dose is 1½ or 2 ounces for a tree ten years old. The solid paradichlorobenzene is placed in a trench or on the surface of the ground, and is covered with earth. Its heavy vapor penetrates downward, and is toxic to insects but not to man. J. S. H.

Mineral Content of Skin.—HERMAN BROWN, of the Research Institute of Cutaneous Medicine (*Jour. Biol. Chem.*, 1926, **68**, 729–736) has determined the calcium, magnesium, sodium, and potassium content of the skin of man, the dog, and the rabbit. The skin of man contains more sodium and potassium than that of either animal, and holds an intermediate position, between the rabbit and the dog, with respect to its content of calcium and magnesium. Distinct differences in mineral content of the skin occur among different species, and individual variability among individuals of the same species. J. S. H.

INTENSIFICATION OF THE LATENT IMAGE ON PHOTOGRAPHIC PLATES AND FILMS.*

I. EXPERIMENTAL STUDY OF LATENT IMAGE INTENSIFICATION.

BY

E. P. WIGHTMAN and R. F. QUIRK.

Research Laboratory, Eastman Kodak Company.

IT WAS shown in some recent work by Wightman, Trivelli and Sheppard,[1] that when single-layer plates were given a flash exposure to light, and were then treated with a solution of hydrogen peroxide, that there resulted an increased developability greater than the sum of the separate light and peroxide effects. The reason suggested for this was that not only developable latent image, but also undevelopable image is produced by light and that the hydrogen peroxide action carries this over into developable latent image, at the same time making its normal proportion of grains developable. This phenomenon may be called intensification of latent image.[2]

Independently of the above work, it was found in connection with some experiments suggested to us by Dr. S. E. Sheppard,[3] that a number of substances produced a considerable latent image intensification on ordinary plates and films as well as an appreciable fog. Some of these substances likewise produced an increased sensitivity to light action, *i.e.*, when used before exposure instead of afterwards.

The purpose of the present work was to study the mechanism of latent image intensification and of latent fog production, and to learn, if possible, the relation, if any, of these effects to the action of light on the photographic emulsion. We have confined ourselves in this first paper, however, largely to an experimental study of the intensifying action of hydrogen peroxide. The intensifying action of silver nitrate is considered briefly.

* Communicated by Dr. C. E. K. Mees, Director, and published as Communication No. 269 from the Research Laboratory of the Eastman Kodak Company.

[1] E. P. WIGHTMAN, A. P. H. TRIVELLI, and S. E. SHEPPARD, JOUR. FRANK. INST., **200**, 335 (1925).

[2] The intensification method described in this paper is largely of scientific interest, and the process requires more care than is ordinarily used in practice.

[3] The results of this have not been published.

I. METHODS AND RESULTS.

1. *The Method of Intensification.*—Strips of plate or film were exposed to light in a Jones sensitometer with steps increasing at a convenient rate, namely, with each step $\sqrt{2}$ times the preceding exposure, nineteen steps in all.

The strips were divided into three groups:

(1) Strips receiving peroxide treatment and water-wash before development.

(2) Strips receiving water treatment for the same time as the combined peroxide and water-wash before development.

(3) Strips receiving only exposure and development and no treatment, *i.e.*, control plates.

In most cases the treated plates were developed without drying, in some they were dried first. Results of both methods are reported below.

Preliminary tests were carried out to find what concentration of peroxide and what time of treatment would give the greatest apparent intensification with the least amount of fog. For this purpose high-speed plates were exposed behind an Eder-Hecht wedge and one-half of each plate in the direction of the wedge was dipped in the peroxide, the concentration of which was varied from 0.004 to 0.016 per cent. The time of treatment was also varied from one to eight minutes with a concentration of 0.004 per cent.

It was found that with the fast plate used, one-minute treatment with 0.008 per cent. peroxide gave about the best results, *i.e.*, practically no more fog than the untreated plate, and a quite strong intensification of the latent image. This time and this concentration were adopted for use in most of the other experiments in which a more accurate sensitometric method was employed.

The plates were exposed and treated as just described. They were then dried and developed for varying lengths of time at 20° in 1:1 pyro-soda developer.[4] Triplicates were run at each time of development, and results were averaged.

[4] Solution A.

Na_2SO_3	70 g.
$NaHSO_3$	17 g.
Pyro	20 g.
H_2O	to 1000 c.c.

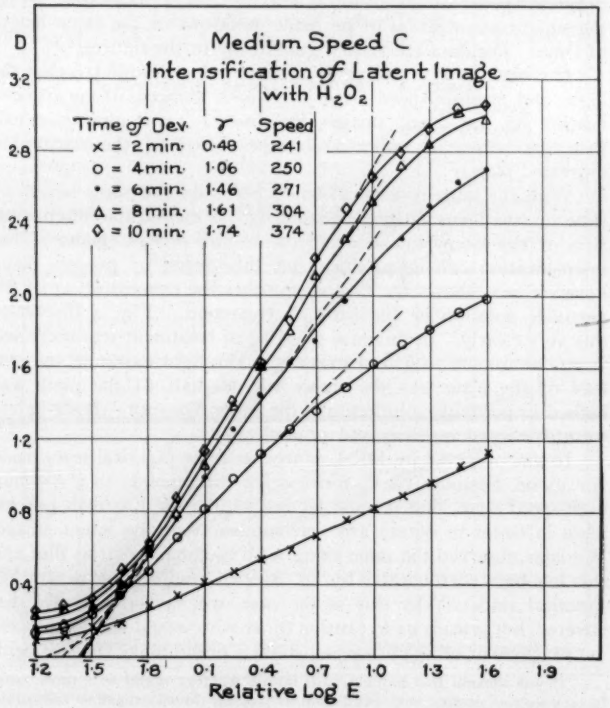
Solution B.

Na_2CO_3	75 g.
KBr	1 g.
H_2O	to 1000 c.c.

When the density data for the various development times were assembled, a family of H. and D. curves was obtained as shown in Fig. 1.

A similar family was of course obtained for both the water

FIG. 1.



treated and for the untreated. From these families, the speeds and gammas or slopes of the straight-line portions of the curves were obtained.

In order to make a better comparison of treated and untreated plates for each development time than by observing the separate

families, the data for each time were replotted together[5] as shown below for plates of different speeds (Figs. 2, 3, and 4).

2. *Intensification and Speed of the Emulsion.*—What relation has latent image intensification to the speed of the plate? To determine this, we treated the latent images on plates of three different speeds—high, medium, and process or slow speed—with the same concentration of peroxide solution for the same length of time. The data are shown graphically in the figures.

It is seen in Figs. 2*A*, 2*B*, 2*C*, and 3*A*, 3*B*, and 3*C*, that the high- and medium-speed plates used both showed strong intensification of the latent image, the former to a greater extent than the latter, as indicated by the ratios of the treated to untreated plates.

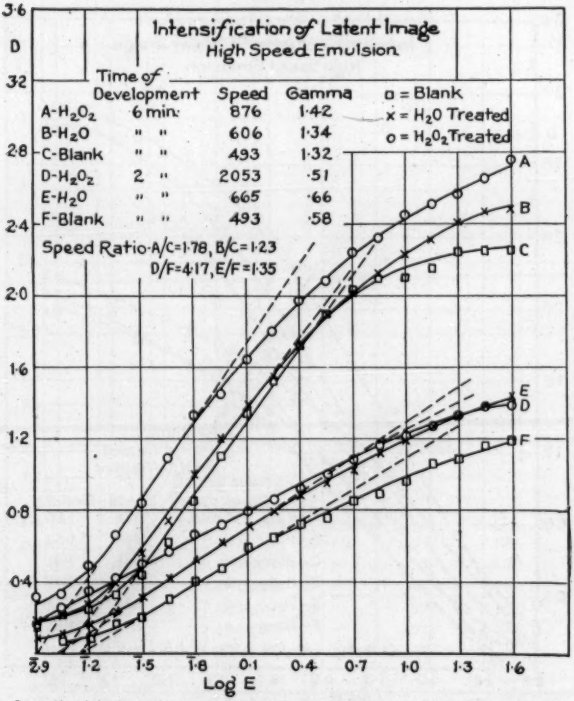
With the same concentration of peroxide and same length of time of treatment as in the preceding, no measurable intensification of the latent image occurred on the process plate. That intensification can be produced on this brand of process plate, however, was shown by increasing either the concentration of the peroxide solution or the time of treatment. Fig. 4 illustrates this very clearly. In this case the time of treatment was increased from one minute to fifteen minutes. The light exposure on each half of the plate was the same, but one-half of the plate was bathed in peroxide solution, and the other was not. Both halves were developed together and printed alike.

It was observed by Mr. Crabtree in some practical tests made for us on Eastman N. C. film, which corresponds to a medium high-speed plate, that it must be treated like the Eastman process plate in order to obtain any intensification of the latent image. We later observed the same thing with Eastman portrait film and this has been corroborated by Dr. Merle Dundon in some further practical tests. Why this is the case, we have not as yet discovered, but it leads us to caution those who would use the process for practical or other purposes to make a preliminary fog test, with

[5] It was thought that plotting each family together would be a more satisfactory way of dealing with the data than plotting directly together the curves of treated and untreated plates for each development time. By this means it is possible (1) to determine the common intersection point, if any, of the extensions of the straight-line portions of the curves for various development times, and (2) to locate possible bad discrepancies, which could then be eliminated either by discarding certain values where the remainder of the data are sufficient, or by replotting the work.

varying concentration of peroxide, of the particular brand of plate or film used before proceeding with the work, otherwise they may either fog their plates or be disappointed by a failure to produce intensification. In other words, while the results obtained above

FIG. 2A.



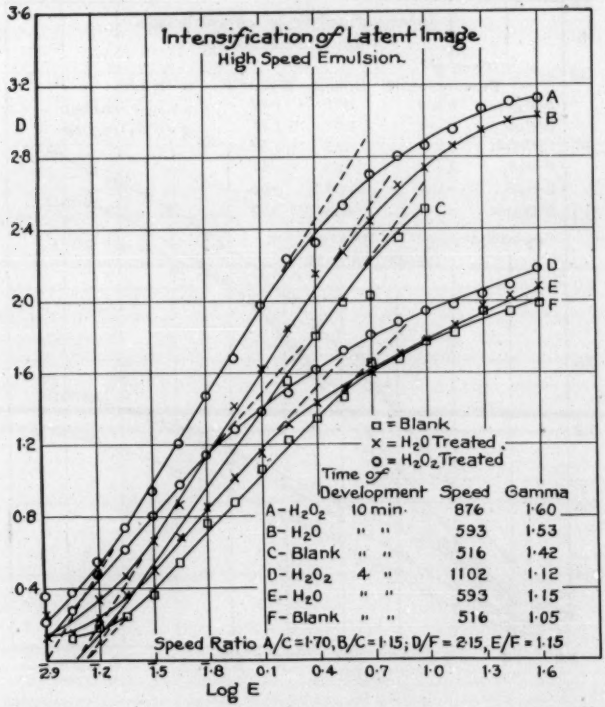
Intensification of latent image on Eastman Speedway plate with 0.008 per cent. peroxide for one minute.

on the various speed plates may be general for most brands of plates of similar speed, and while most film may behave as that we have used, we do not wish to commit ourselves to such a general statement.

As noted above, for every plate treated with peroxide, there

were two control plates, one treated with water for the same time as the peroxide treatment, and one untreated. Those treated with water showed an increased developability of the latent image lying somewhere between the developability of the untreated and

FIG. 2B.



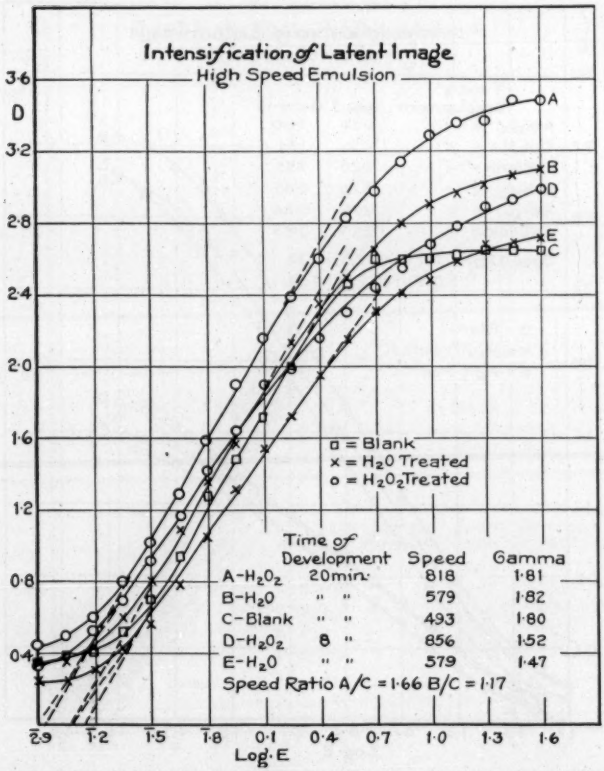
Intensification of latent image on Eastman Speedway plate with 0.008 per cent. peroxide for one minute.

of the peroxide-treated plate. This fact, that water produces an increased developability of latent image, has been known for some time but has not received any special attention. We believe it to be a different effect from the phenomenon which we have

called latent image intensification. Our reason for this will be considered later.

As to the experimental facts, the water effect was usually

FIG. 2C.

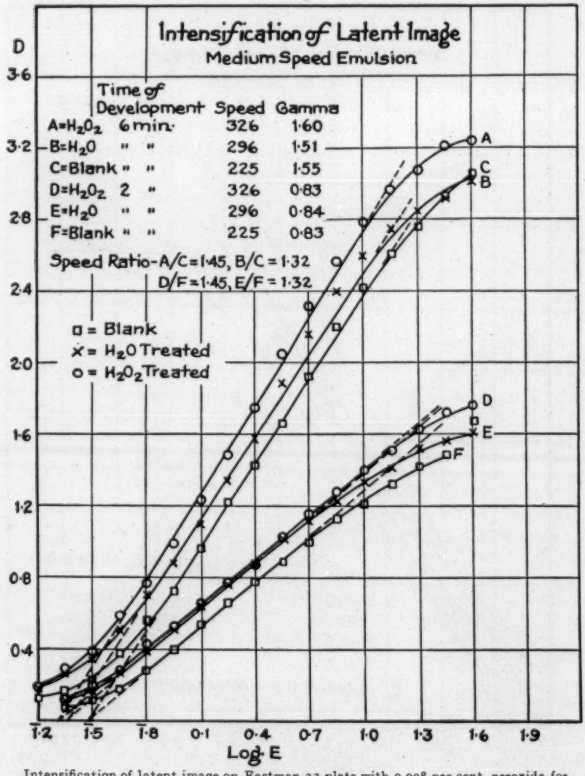


Intensification of latent image on Eastman Speedway plate with 0.008 per cent. peroxide for one minute.

stronger for short times of development than for long, in some cases, indeed, becoming practically negligible when the development time reached twenty minutes (Figs. 2*C* and 3*C*).

Development fog and the effect due to water were not subtracted from the peroxide-treated data. To find the effect due to the peroxide alone, some correction should of course be made.

FIG. 34.



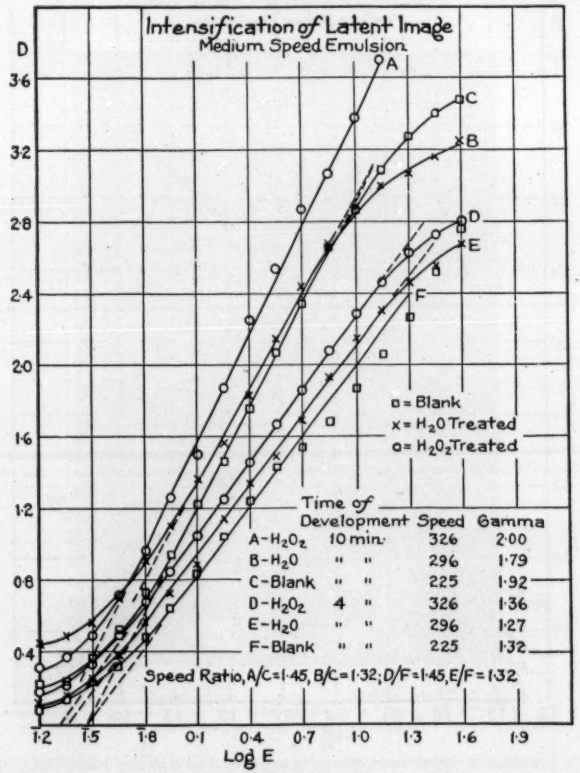
Intensification of latent image on Eastman 33 plate with 0.008 per cent. peroxide for one minute.

But simple subtraction throughout the density-exposure range is not sufficient.[6]

[6] *Cf.* R. B. WILSEY, *Phot. J.*, 65, 454 (1925).

Correcting for fog alone is a complicated procedure, and adding another correction does not simplify it, so that it was thought best to give the data as determined.

FIG. 3*B*.

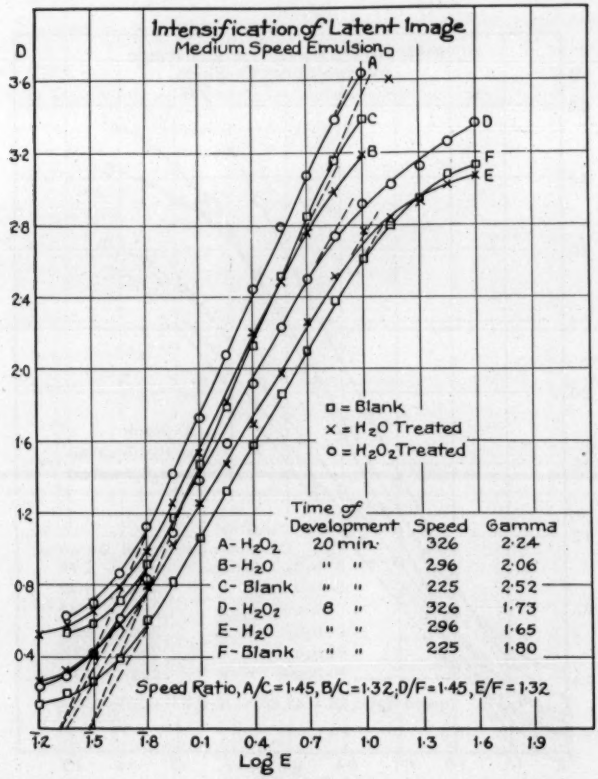


Intensification of latent image on Eastman 33 plate with 0.008 per cent. peroxide for one minute.

3. *Intensification of Latent Image on Desensitized Plates.*—When high-speed plates are desensitized with CrO_3-H_2SO_4

solution as previously described [7] it is believed that most, though not all, of the sensitivity spots are removed by the desensitizer. It

FIG. 3C.



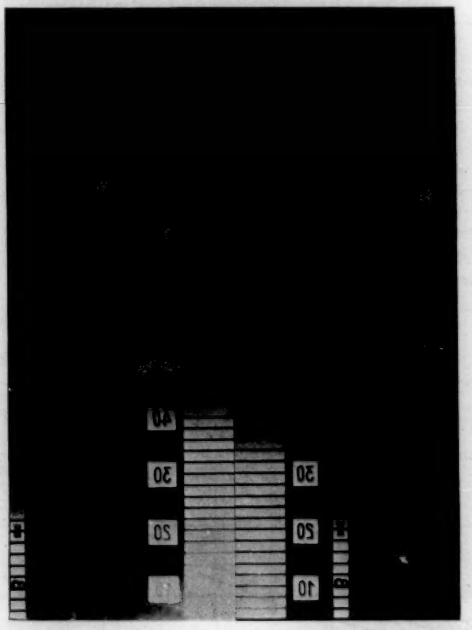
Intensification of latent image on Eastman 33 plate with 0.008 per cent. peroxide for one minute.

should therefore be possible to produce little or no latent fog by

[7] S. E. SHEPPARD, E. P. WIGHTMAN, and A. P. H. TRIVELLI, JOUR. FRANK. INST., 196, 788 (1923).

peroxide, provided the sensitivity specks are the centres of activity. On exposure of the desensitized plate to light, the latent image must consist largely of new spots produced by the light action. Whether this is similar to the condition existing in a

FIG. 4.



0.008 per cent. H_2O_2 for fifteen minutes. Blank. No treatment.

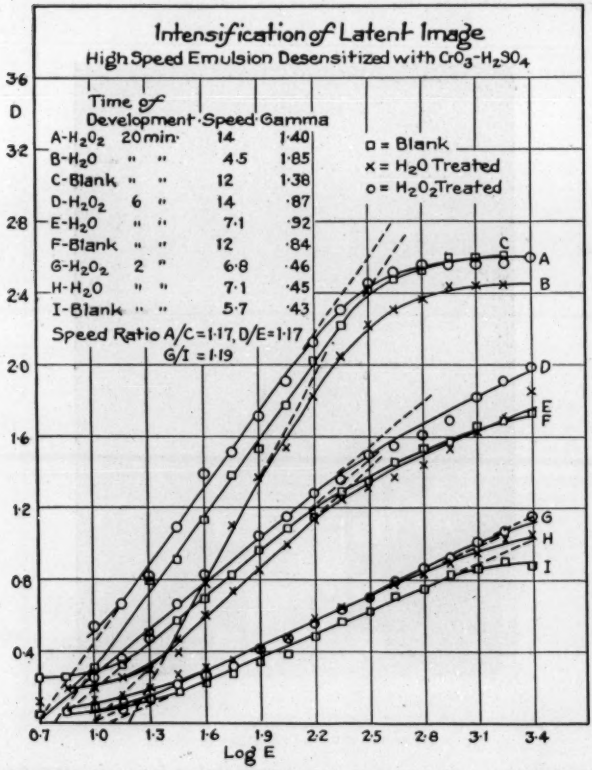
Process Plate.
Comparison of treated and untreated plates.

process plate we are not prepared to say, but it is of interest to know how the action of peroxide on the latent image compares in the two cases.

Eastman Speedway plates were desensitized and exposed for us by Mr. E. Huse in a Jones sensitometer. The exposure series

used was 64 times the normal one for a high-speed non-desensitized plate. On treating a set of these desensitized plates with

FIG. 5.

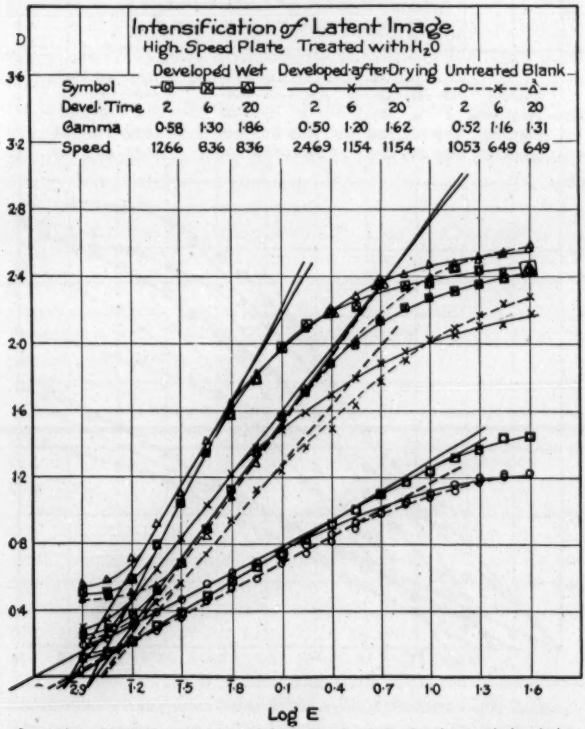

Intensification of Latent Image
High Speed Emulsion Desensitized with CrO_3-H_2SO_4
Time of Development Speed Gamma
A-H_2O_2 20 min. 14 1·40
B-H_2O " " 4·5 1·85
C-Blank " " 12 1·38
D-H_2O_2 6 " 14 ·87
E-H_2O " " 7·1 ·92
F-Blank " " 12 ·84
G-H_2O_2 2 " 6·8 ·46
H-H_2O " " 7·1 ·45
I-Blank " " 5·7 ·43
Speed Ratio A/C = 1·17, D/E = 1·17
G/I = 1·19
□ = Blank
× = H_2O Treated
○ = H_2O_2 Treated
D
Log E

Intensification of latent image on a desensitized Eastman Speedway plate with 0.3 per cent. peroxide for four minutes.

peroxide it was found that they behaved in a similar way to the Eastman process plate in not being affected by the more dilute peroxide. In like manner, they did show some intensification of

latent image when the peroxide was sufficiently concentrated. The concentration, however, was the equivalent of about ten times that required for the process plate, being 0.3 per cent. peroxide for four minutes instead of 0.008 per cent. for

FIG. 6A.

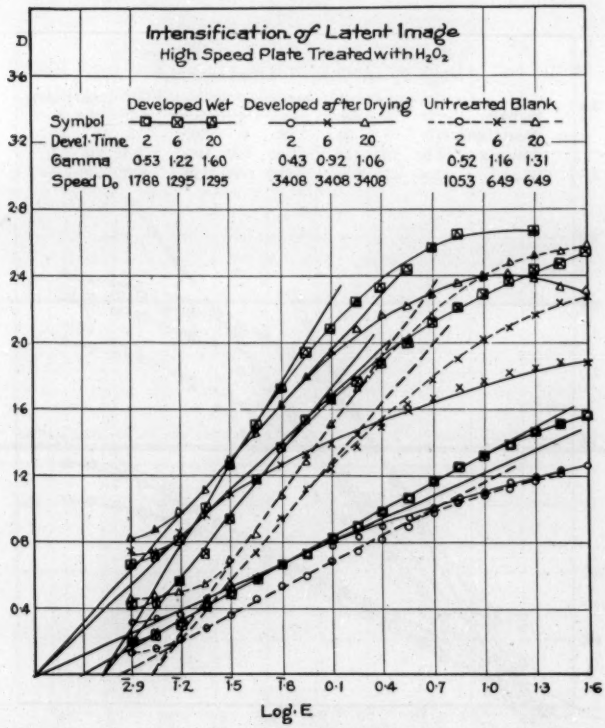


Comparison of intensification of latent image when plate is developed wet and after drying.

fifteen minutes. Fig. 5 shows the result of this experiment. The curves for water treatment were quite erratic and the data in general were not so concordant as in the cases of the non-desensitized emulsions.

As for the production of latent fog, strips of the desensitized plates were dipped for about one-third their length in peroxide solutions of concentrations varying from about 0.01 to 3.0 per

FIG. 6*B*.



Comparison of intensification of latent image when plate is developed wet and after drying.

cent. and for times from one minute to one hour. In no case was a density above 0.3 obtained.[8] A concentration as high as 1 per cent. acting for one minute was necessary to produce the least

[8] *Cf.* E. FUCHS, *Phot. Ind.*, p. 56, 649 (1924). Fuchs noticed that peroxide did not produce a latent fog effect on plates treated with desensitizing dyes.

perceptible fog. A concentration of 0.3 per cent. acting for four minutes gave approximately the same result. Compare this with the effect of the 0.008 per cent. solution for one minute in the case of non-desensitized plates. Reversal took place with a concentration of 3 per cent. peroxide solution and a time of treatment longer than one-half hour.

4. *Effect of Drying a Plate after Intensification.*—For practical purposes it is more advantageous to intensify the latent image immediately before development and not to dry the plate after the intensification. Since some preliminary experiments indicated a difference in the results from the two methods, and since it was thought possible that some light might be thrown on the question of the water effect by a comparison of them, two parallel series were run with a high-speed emulsion.

Figs. 6*A* and 6*B* show the result. One sees first of all that the curves for each development time in the case of the plates not dried after treatment, *i.e.*, of plates developed wet, are quite a bit steeper than those for the plates dried after treatment. Secondly, the treated and dried plates were considerably faster than the treated and undried ones.

One peculiarity noted is that the dried peroxide-treated plate developed for twenty minutes showed a distinct maximum in the shoulder of the curve. This phenomenon seems to happen now and then, but not always with high-speed plates developed for a long time. We do not believe this to be a true reversal effect. However, the fog caused by the peroxide and water in this series was somewhat higher than usual and it is possible that the treatment (although the same as in the previous work) was somewhat excessive. In other words, just as different batches of the same brand of plate vary somewhat in speed, so also they vary in the degree to which they are affected by peroxide and by water.

The data under headings 2, 3 and 4, showing the relation of intensification of the latent image to type of plate and method of treatment, are summarized in Tables I and II (see Figs. 7 and 8). The term " Speed " in Table I, as applied to the plate with intensified latent image, means, of course, the result after treatment and was used simply for lack of a better term.

The percentages given in Table II were calculated without fog correction. When fog as determined from the developed step

exposure strips is subtracted from the densities in the toe region of the treated and untreated plates, the percentage values are then considerably greater than those in the table for the very low-exposure region. In fact, with decreasing exposure they approach infinity. As exposures increase, fog correction becomes

TABLE I.

Relation of Latent Image Intensification to Type of Plate and Mode of Treatment.

Plate.	Treatment.	Ratio of Speed of Treated to That of Untreated Plate.* Time of Development in Minutes.					
		2	4	6	8	10	20
Eastman Speedway †	Control— No treatment	1	1	1	1	1	1
	H_2O	1.35	1.15	1.23	1.18	1.15	1.17
	H_2O_2	4.17	2.15	1.78	1.74	1.70	1.66
Eastman 33 †	Control— No treatment	1	1	1	1	1	1
	H_2O	1.32	1.32	1.32	1.32	1.32	1.32
	H_2O_2	1.45	1.45	1.45	1.45	1.45	1.45
Eastman process †‡	Control— No treatment	1	1	1	1	1	1
	H_2O	1	1	1	1	1	1
	H_2O_2	1	1	1	1	1	1
Desensitized Speedway §	Control— No treatment	1		1			1
	H_2O	1.25		0.59			0.38
	H_2O_2	1.19		1.17			1.17
High speed ‖	Control— No treatment	1		1			1
Developed wet	H_2O	1.20		1.29			1.29
	H_2O_2	1.70		2.00			2.00
Developed dry	H_2O	2.34		1.78			1.78
	H_2O_2	3.24		5.25			5.25

* No comparison is made of the speeds of the control plates at different development times, but the speed of these was in each case chosen as 1.

† The concentration of peroxide was 0.008 per cent. and the time of treatment one minute.

‡ The speeds in this case were not actually determined since they were all practically the same within the limits of error.

§ The concentration of peroxide was 0.3 per cent. and the time of treatment four minutes. The water-treated plate was very erratic, having a speed above that of the control at two minutes and below that of the control at six and ten minutes' development time.

‖ Concentration of peroxide was 0.008 per cent., and time of development one minute.

less and less and hence the percentages given in the table represent more and more nearly the true percentage increase of density with treatment.

It is of special interest to note that in the intermediate exposure region of both the fast and slow plates the percentage density

increase is about the same within the limits of experimental error for nearly all times of development.

Another interesting point is that while the intensification as expressed by the percentage values decreases continuously with increasing exposure for the slow plate and desensitized plate, it passes through a minimum for the longer development times on

TABLE II.

Intensification of Latent Image Expressed as Percentage Increase in Density with Varying Exposures and at Different Development Times.

Relative Log E.	Eastman Speedway. Percentage Increase in Density at Development Times (in minutes) =						Eastman 33. Percentage Increase in Density at Development Times (in minutes) =						Speedway; Desensitized Percentage Increase in D at Dev. T. =
	2	4	6	8	10	20	2	4	6	8	10	20	20
$\bar{2}.90$	193	83	67	43	35	27	..	...	...	..	..	..	...
$\bar{1}.05$	278	144	74	77	59	44	..	...	...	..	..	..	...
$\bar{1}.20$	258	150	79	86	75	51	60	113	100	92	63	31	...
$\bar{1}.35$	190	148	90	84	77	54	57	77	80	76	54	25	...
$\bar{1}.50$	136	100	77	77	70	52	55	70	58	56	47	23	...
$\bar{1}.65$	90	76	58	60	55	41	50	53	49	49	41	21	...
$\bar{1}.80$	65	61	44	48	41	31	39	44	43	47	43	21	...
$\bar{1}.95$	52	47	36	41	35	26	25	35	38	40	39	24	...
0.10	41	36	29	33	30	22	19	29	30	31	31	21	59
0.25	35	26	21	28	26	18	15	24	25	26	26	17	31
0.40	32	20	15	22	21	14	13	20	22	22	22	14	21
0.55	28	15	12	17	16	14	11	18	19	20	20	11	16
0.70	26	13	11	15	16	17	10	18	17	18	18	9	13
0.85	25	11	12	16	17	21	9	17	16	15	17	7	12
1.00	23	10	13	18	18	24	8	18	15	12	(17)*	6	10
1.15	22	10	14	20	20	28	7	17	14	10	(19)	4	9
1.30	20	9	17	21	21	30	6	14	12	8	(20)	4	7
1.45	19	8	18	23	23	31	4	11	7	7	(19)	3	4
1.60	17	8	20	24	24	32	3	7	6	6	(17)	1	2.0
1.75	...	...	..	..	..	..	..	..	..	..	..	..	1.0
1.90	...	...	..	..	..	..	..	..	..	..	..	..	0.6
2.05	...	...	..	..	..	..	..	..	..	..	..	..	0.1
2.20	...	...	..	..	..	..	..	..	..	..	..	..	0
2.35	...	...	..	..	..	..	..	..	..	..	..	..	0
2.50	...	...	..	..	..	..	..	..	..	..	..	..	0

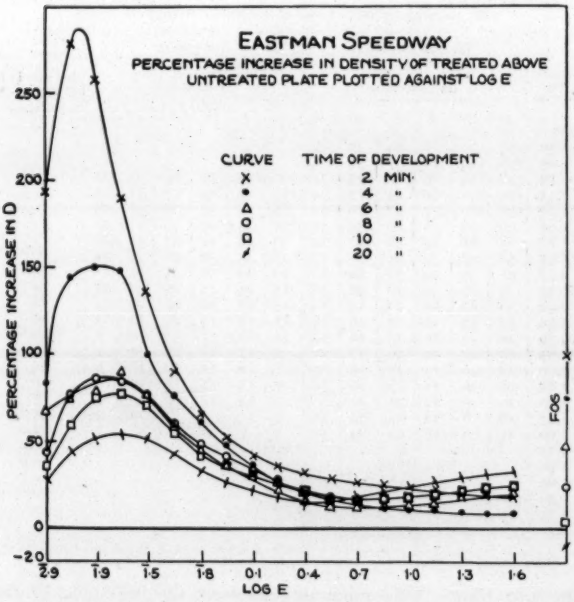
* Values in parenthesis are very uncertain.

the fast plate. This minimum lies near the beginning of the shoulder of the D-log E curve. Now it may be seen from Figs. 2*B* and 2*C* that the curves of untreated fast plates take a sharp bend when the shoulder is reached and then show very little increase, whereas the curve of the peroxide-treated plate rises higher and does not come so quickly to the maximum value. This probably indicates that all of the grains of the untreated plate are not made developable even with prolonged exposure, whereas

they are made developable by peroxide treatment, or that the photometric constant is affected markedly by the peroxide treatment due to change of size of grains on development. The latter is very unlikely.

5. *Intensification of the Latent Image Produced by Light Transmitted through Tricolor Filters.*—The question arose, is

FIG. 7.



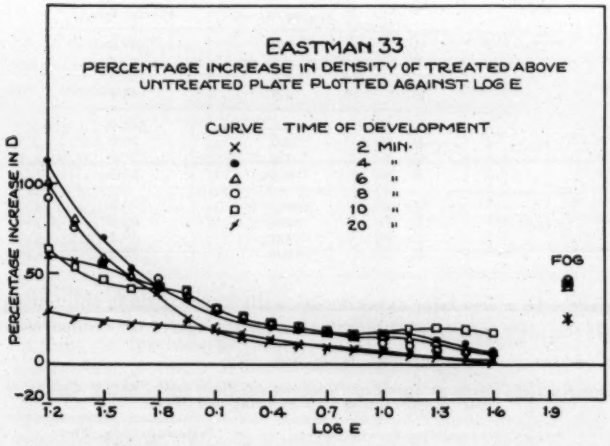
there a differential intensification of the latent images produced by light of different wave-lengths? To test this, panchromatic plates were exposed for us by Mr. E. Huse in a Jones tricolor sensitometer. They were intensified in the manner already described (with 0.008 per cent. peroxide for one minute) and developed, etc. Table III gives the average speeds of the variously exposed plates at density, $D = 0.0$ and at $D = 1.0$.

When the speeds of the control (untreated) plates are taken as 100 per cent., it then may be seen what effect the intensification had on the plates exposed to white, blue, green and red light. The results are given for both $D = 0.0$ and $D = 1.0$ in Table IV.

There was a marked intensification of panchromatic plates by both water and peroxide when speeds were determined at $D = 1.0$, but when obtained at $D = 0.0$ in the usual way, intensification was much less with peroxide and practically negligible with water.

While the blue appears to have been more intensified by per-

FIG. 8.



oxide than the white, green and red, the difference lies within the limits of error in this experiment.

6. *Intensification by Other Substances Than Hydrogen Peroxide.*—When the work was started on intensification it was at first thought that this phenomenon was a general property of all substances which had a tendency to produce latent fog, so a number of such substances were tried at such concentrations that latent fog was hardly perceptible, *i.e.*, in the same way as peroxide was used. Among those tried were ammonia, some amino compounds such as aniline and allyl thiourea, sodium thiosulphate, methylene blue, carbon disulphide in benzene and some others.

The tests were made by exposing Eastman 40 plates uniformly behind an Eder-Hecht wedge and treating them for two and one-half hours with the various substances and comparing them with an untreated plate. The results obtained in degrees Eder-Hecht are given in Table V.

This, of course, gives only the values for the least perceptible

TABLE III.

Average Speed for Light of Various Colors, of Plates with Latent Image Untreated, Peroxide-treated, and Water-treated.

Material.	Light.	$D = 1.0$ Average Speed.	$D = 0.0$ Average Speed.
Control	W	52.9	581.0
	B	5.1	76.5
	G	2.9	30.5
	R	3.5	24.0
H_2O	W	89.9	514.0
	B	9.6	79.0
	G	5.4	31.0
	R	6.5	27.5
H_2O_2	W	102.7	700.0
	B	10.6	95.5
	G	5.6	36.5
	R	6.0	28.5

image. In a few later experiments with some of these substances half the plate was treated lengthwise, so as to have the comparison

TABLE IV.

Comparison of Percentage Speeds of Panchromatic Plates with Tricolor Exposures and Intensification with Peroxide and Water.

Material.	Percentage Speed When $D = 1.0$.				Percentage Speed When $D = 0.0$.			
	W.	*B.*	*G.*	*R.*	*W.*	*B.*	*G.*	*R.*
Control	100	100	100	100	100	100	100	100
H_2O	160	188	186	186	...	103	102	115
H_2O_2	194	208	193	171	120	125	120	119

strip side by side with the treated, and to be able to follow the result through the whole density series. The concentrations were increased and the time of treatment decreased and so adjusted by trial that practically no fog was produced other than the normal amount due to development. Under these circumstances ammonia and allyl thiourea produced only a very slight, if any, intensifica-

tion, and formaldehyde a lessening of developability possibly due to its hardening action.

So far, no substance tried, with one exception, has proven anywhere nearly so powerful as peroxide in producing intensification of the latent image when used under the same simple conditions. This exception is silver nitrate, which was not considered in the above list because of its importance.

7. Action of Silver Nitrate on the Sensitivity and on the Latent Image.—It has been known since the earliest days of the dry plate photography that when silver bromide is precipitated

TABLE V.

Intensification by Various Substances; Time of Treatment 2.5 Hours.

Substance.	Concn.	Degrees Eder-Hecht.	Approx. Speed Increase.	Fog.
Control	.....	76	1	.....
CS_2 in C_6H_6	1: 1,000	88	3.1	Moderate
Pure C_6H_6	.....	80	1.5	None
$C_6H_5NH_2$ in H_2O	1: 100,000	72	−1.5	None
HCHO in H_2O	1: 100,000	86	2.5	Moderate
NH_3 in H_2O	1: 100,000	84	2.1	Moderate
$Na_2S_2O_3$ in H_2O	1: 1,000,000	80	1.4	Moderate
Na_2S in H_2O	1: 1,000,000	78	1.2	None
H_2O_2 in H_2O*	1: 10,000	86	2.5*	Moderate

*Time of treatment‡ for only 1 minute.

in an excess of silver nitrate, even when very thoroughly washed, it fogs on development without previous light exposure. Obviously then, if a plate is bathed in a sufficiently concentrated silver nitrate solution, it will do the same thing as soon as the trace of potassium bromide which it normally contains is used up, by transformation into silver bromide. A trace of silver nitrate below equivalence to this potassium bromide, however, will increase sensitivity without fog production.

The power of silver ions to produce developability without light exposure is of interest, and has been dealt with adequately by others. From the standpoint of the present work, it is of importance, as will be seen later, to know whether or not the presence of excess silver ions on the exposed silver halide grain will increase developability above that produced by light, without at the same time causing increased latent fog.

Mr. J. G. Capstaff and Mr. E. R. Bullock, in this laboratory, previously in another connection, tried the effect of silver nitrate

solution on the latent image. Their results were not very concordant and were never published, but they produced on some plates an increased developability of the latent image.

Owing to the uncertainty of their results, we carried out some further experiments in a similar way to our preliminary tests with peroxide. Eastman Speedway plates were exposed behind an Eder-Hecht wedge and bathed in varying concentrations of silver nitrate solution from 0.05 to 0.0063 per cent. for ten minutes. They were then washed in running water ten minutes, developed in 1 : 1 pyro-soda developer for five minutes, at 20°, and fixed, washed, and dried as usual. The washing is essential in order to remove excess silver nitrate from the gelatin, since silver nitrate in solution is immediately reduced to silver by developer.

At the upper concentration bad fog resulted—the excess silver nitrate not absorbed to the grains had not been completely washed out and was reduced by the developer. At the concentration of 0.025 per cent. the fog was negligible and a strong intensification, amounting to 10° E.H. in the threshold value and an increased developability throughout the exposure series was obtained. With a concentration of 0.0063 per cent. there was still an appreciable intensification. No attempt was made to find the least concentration at which an intensification was obtainable.

We have not tried the intensifying action of other soluble silver salts or of the soluble noble metal salts in general on the latent image, but it is very likely that they would behave similarly to silver nitrate. So far as our experiments have gone, however, peroxide and silver nitrate, as we have stated, seem to be unique among the substances producing intensification of the latent image, in that they are the only ones yet found which give strong intensification in a short time, when the concentration is low enough not to produce objectionable fog.

8. *The Least Amount of Hydrogen Peroxide Detectable by the Latent Image Intensification Method.*—When it is known that there are no other impurities in a given solution that might produce intensification or destruction of latent image, it is possible to determine exceedingly minute quantities of peroxide in the solution by this method. We have found by experiment, in fact, that as little as 1 part in 10,000,000 of water can be determined to within 20 to 30 per cent.

The method consists of exposing several 4 × 5 Eastman

Speedway plates alike behind an Eder-Hecht wedge so that if developed, the threshold value would be about 60°. The plates are cut in half lengthwise and one half is bathed for say ten minutes in the solution to be tested and the other half in a peroxide solution of known strength and after a brief rinse in water, these and an untreated half of a second plate are developed together for two minutes in 1 : 1 pyro-soda developer at 20°. After fixing and brief washing (drying is not necessary), the differences in threshold values on the two treated halves and on the control plate are determined. Another half plate treated in the unknown solution is then compared in the same way with a known solution of different strength, which of course gives a different threshold value from the first. If the unknown lies between these two, then its strength is easily estimated, if not, then a third determination can be made in a similar manner, with a longer or shorter time of treatment and so on until two knowns are found which give readings on each side of the unknown. If the experimental method is accurately controlled as to temperature, concentration, and other factors, then as long as plates of the same emulsion numbers are being used for the tests, it is not necessary to repeat the control halves with each unknown, provided a complete series of knowns has been determined in advance. For concentrations greater than 1 : 50,000, ten-minute treatment of the latent image is sufficient; for those from 1 : 50,000 to 1 : 500,000, 100-minute treatment should be used; for those from 1 : 500,000 to 1 : 5,000,000, 1000-minute treatment is necessary. Smaller concentrations can be detected at this last time, but it is better to use about a 2000-minute treatment.

II. DISCUSSION OF RESULTS.

In the latent image intensification hypothesis mentioned at the outset, it was assumed that the intensification depended upon the undevelopable latent image spots, upon those altered by light but not sufficiently so to become developable. Since it is probable that there are on the average both more sensitivity spots and larger ones present on the larger grains in high-speed plates than in low-speed ones,[9] it is very probable that a larger per cent. of these in the former would be brought by light to the intermediate stage

[9] SHEPPARD, TRIVELLI, and LOVELAND, JOUR. FRANK. INST., 200, 335 (1925).

just below developability than in the latter. Those fewer ones in the latter, below the developable level, *would be further below* because they had to start from a smaller size; and *hence a greater concentration of the peroxide* (or longer time of action) *would be necessary to bring them up to the developable condition.* This is borne out also by the fact that a greater concentration of peroxide than that used for intensification of latent image is necessary to produce increase of sensitivity in a high-speed plate. The sensitivity specks obviously are smaller than the latent image spots, but they both have to be raised to the same level (*i.e.*, increased to the same size) in order to be developable in the same developer.

It was noted above that no matter what the concentration of peroxide (below that which would produce fog), a less intensification was produced on the lower speed than on the higher speed plates. This was shown in the case of desensitized plates to be due to a reversal effect brought about by the excessive peroxide treatment. In the case of high-speed plates, a reversal effect is produced with only slight excess of peroxide treatment (Fig. 2). It is probable that the same kind of effect occurs on low-speed plates with a similar treatment. It will be remembered that in the work of Wightman, Trivelli and Sheppard on single layer plates that large grains appeared to be less affected by peroxide than intermediate and small grains. The treatment given was somewhat excessive so it is quite possible that this was a case of reversal on the larger grains.[10]

When a plate is treated for only one minute with a peroxide solution, it appears certain that the peroxide has not produced as much effect on the grains next to the glass plate as on those at the surface. It is evident, therefore, that the difference in gamma between treated and untreated plates is comparatively large for short times of development, and it would tend to become less marked or even disappear altogether as the time of development increases.

For the same reason, the speed ratios of treated to untreated

[10] A paper by W. CLARK, *Phot. J.*, 66, 78 (1926), has just appeared, in which evidence is given that large grains in a pure bromide emulsion are more affected by peroxide than the small ones, supporting Svedberg's previous result on Agfa Special Emulsion.

plates are greater for the short development times than for the longer times.

There may be some other factors in connection with the above-mentioned effects, but they play a minor part.

It is possible that these variations in the gamma differences between treated and untreated plates for short and long times of development might be eliminated by treating for a sufficiently long time with a much more dilute peroxide solution. This we have not yet tried. It is also possible that with such a method of procedure a greater degree of intensification could be obtained.

In almost all of the experiments described, we treated one set of plates with water side by side with those treated with peroxide and it was noticed that water produces an apparent intensification. The peroxide effect as given included the effect of the water. Sometimes the water effect was not as marked as at others. It is believed that this water effect is not entirely an intensifying action. As is well known, water swells the emulsion and allows developer to penetrate, and hence increases the rate of development. Even when the emulsion was to all appearances dried after treatment there was more moisture present in it than prior to treatment because the time of drying was comparatively brief and the emulsion had not been brought to standard temperature and humidity conditions.

It has been known for a long time that flash exposures not sufficient to cause appreciable fog produce increased sensitivity. Considerable work has been done on this and we shall not attempt to quote it here. It is of interest to note, however, that Messrs. J. G. Capstaff and Newton Green in some unpublished experiments found that the flash exposures given after, as well as before, the step exposures increased developability. The greatest effect was produced on positive film and clean working plates and was a maximum when the flash exposure equaled that at the beginning of the straight-line portion of the D-log E curve. The method had no practical advantage, however, because of the lens flare in the camera.

We have not, in this paper, considered the mechanism of the peroxide action in producing intensification of the latent image. We have reserved this discussion and some experiments which have to do with the mechanism, for a second paper which will appear shortly.

ACKNOWLEDGMENT.

The writers wish to thank Dr. C. E. K. Mees, Director of this laboratory, and Dr. S. E. Sheppard, Assistant Director, for helpful suggestions and criticisms in connection with this work. They also wish to acknowledge their indebtedness to Mr. Emery Huse for photographic exposures on the Jones sensitometer and for numerous density measurements.

SUMMARY.

(1) Hydrogen peroxide and silver nitrate, and possibly other soluble noble metal salts acting on a photographic plate after exposure and before development increase the developability of the light-exposed portion above its normal developability and in greater proportion than that of the unexposed portion. This we have called intensification of the latent image.

(2) Hydrogen peroxide and the salts just mentioned seem to be unique among the numerous substances we have used for producing intensification of the latent image, in that they are the only ones which give a strong intensification when the concentration is low enough not to produce objectionable fog. This effect is, however, approximately equivalent in degree to that produced by a brief flash exposure of the plate to light before or after the principal exposure.

(3) With the same concentration of hydrogen peroxide and time of treatment, the latent image on the fast plates which we have used was affected to a greater extent than on medium-speed plates, while on the process and desensitized plates used it was not affected at all. Eastman portrait and N. C. films behaved like the process plates.

(4) The latent image on the process plates, desensitized plates, and the film just mentioned could be intensified to a certain extent by increasing the hydrogen peroxide concentration, or by lengthening the time of treatment over that used for the fast plates.

(5) It was possible to produce no more than a slight latent fog with hydrogen peroxide, *i.e.*, with no light exposure, on desensitized plates, no matter what concentration or time of treatment were used.

(6) Water caused an apparent intensification of the latent image. This is explained as partly due to swelling of the gelatin, allowing more rapid penetration of developer.

(7) The ratio of gamma of the peroxide-treated to the untreated plates usually increased with increasing development time.

(8) Intensification of latent image in most cases increased somewhat with increasing development time when measured as a density effect and decreased when measured by H. and D. speed difference.

(9) Experiments have shown that as little as 1 part hydrogen peroxide in 10,000,000 of water can be determined to within 20 to 30 per cent. by the latent image intensification method, when it is known that other intensifying agents and oxidizing substances are not present.

(10) The hypothesis, previously stated by Wightman, Trivelli and Sheppard, that light produces not only a developable but also an undevelopable latent image, and that the peroxide action makes this latter image developable in producing latent image intensification is supported by the present work. An extension of this hypothesis has been found necessary to explain the action on the latent image of fast, medium and slow plates, namely, that there is less undevelopable image formed by light in the medium and slow plates and desensitized high-speed plates and it is for this reason that the same concentration of peroxide and same time of treatment give different degrees of intensification on these plates of different speed.

Snow Removal Cheaper Than Clogged Roads.—Highway officials in thirty-six "snow states" report a program of open roads for the snow season of 1926–1927 aggregating 92,756 miles. In the winter of 1925–1926 the road mileage cleared of snow in these states was about the same, compared with 62,165 miles in the winter of 1924–1925. Their expenses for snow removal work last winter were in the neighborhood of $4,000,000. Enthusiasm for keeping roads open for winter traffic is so keen in some states that taxpayers insist on snow removal even if the funds required for that purpose curtail road construction work.

Formerly the movement of farm products to the cities was discontinued during the winter months and necessary commodities were procured for consumption by country people in the fall. Country storekeepers, especially those doing business at a distance from railroad stations, had to stock up before the first snowstorm, and were saddled with a heavy investment for holding merchandise until required by consumers. This condition lasted until motor

vehicles came into general use and the rural public began to call for improved roads.

It soon came to be realized that improved roads did not yield anything like the maximum possible return on the investments made in them unless they were open to traffic during the entire year. It was also felt that costly motor vehicles, without roads to carry them, tied up much capital unprofitably.

So strong is the demand from taxpayers for more extensive snow removal programs that the Department of Agriculture believes it will not be many years before all paved roads and their connecting sections in the United States will be kept open for year-round traffic. Accordingly, the department is studying snow removal expense in various states to ascertain the best and cheapest methods. Straight-blade and V-shaped plows mounted on speed trucks are extensively used. New Jersey, with an average annual snowfall of 31.8 inches and about 1270 miles of road to be kept open, uses the straight-blade, truck-mounted plow almost exclusively. For opening drifts or packed sections of roadway, or for widening roads already made, powerful displacement plows with tractors, and various types of rotary plows, are employed. Operating costs are lower for truck plows than for tractor plows. Newly fallen snow to a depth of nine inches, and short sections of snow recently drifted but not packed or crusted, can be efficiently removed with truck plows. The Department observes that snow rarely falls at one time to a depth greater than nine inches. Indeed, the greater number of storms deposit only from two to five inches of snow. Storms depositing five and seven inches or more are comparatively rare. Snowfall depths are often greatly exaggerated.

Costs of snow removal vary in different localities. The frequency, general direction and strength of the prevailing winds are important factors. An area in such a position as to be protected from heavy winds, or having its main roads parallel with the general direction of the wind, may keep the cost of snow removal to the minimum. Areas in open country with main roads running in a direction that makes drifting inevitable, may have much heavier costs. Whether the snow is moist or dry is another cost factor, dry snow being naturally cheaper to remove. Snow falling to a depth of seven inches without wind can be removed at low cost before it has settled or become packed. After it has settled or become packed and drifted, the cost of snow removal is much greater.

New Deposits of Borates.—L. F. NOBLE (U. S. Geol. Survey, *Bulletin 785 C*, 1926, 45–61) describes the occurrence of deposits of ulexite (a calcium sodium borate) and colemanite (a hydrous calcium borate) in upper Miocene strata near Kramer, Kern County, Calif. The same author (U. S. Geological Survey, *Bulletin 785 D*, 1926, 63–73) describes an unusually rich deposit of colemanite near Shoshone, Calif., in strata of Tertiary age. Both fields are being worked. J. S. H.

SPACE CHARACTERISTICS OF ANTENNÆ.*

BY

WILLIAM H. MURPHY.

Captain, Signal Corps, U.S.A.

IN THE first article on this subject (JOURNAL OF THE FRANKLIN INSTITUTE, April, 1926) we discussed and developed formulæ for the electrostatic fields in space due to various antennæ and simple combinations of the same, the true fields being resolved into three geometric components, E_1, E_2, and E_3, corresponding with the vertical, or Z', axis through the point under consideration, the horizontal, or X', axis in the plane of propagation, and the horizontal, or Y', axis at right angles to the plane of propagation (see Figs. 3 and 5 of the original article).

INDUCED VOLTAGES.

(1) *The Receiving Antenna.*—As stated in the previous article, we may at times not be interested in the total field, but merely in one of the resolved component fields; this is clearly the case if we consider the voltages induced in a vertical antenna in which the only field component of interest is the vertical, or Z', component E_1. Such a field will obviously induce a voltage proportional to the height of the antenna in question and we can express this voltage as $E_1 = kE_1h_2$, where k† is $\mathfrak{E}/E_1$, $\mathfrak{E}$ being the voltage gradient of the field in volts per centimetre and h_2 the effective antenna height in centimetres. Assuming k at unit distance, and the height h_2 to be unity, we can write $E_1 = E_1$. In a similar manner we can express the voltage induced in a horizontal antenna parallel to field E_2 as E_2 and in a horizontal antenna parallel to E_3 as E_3, we can in fact write the resultant voltage as E in each case as the remaining two fields will each induce zero voltage in the antenna in question. The total voltage is the algebraic sum of the three component voltages so that $E = E_1 + E_2 + E_3$.

Let us now consider the receiving antenna to be a horizontal dipole antenna which, however, does not necessarily correspond with the X' or Y' axis but departs from the latter (Fig. 11) by the angle θ_2, the angle being measured clockwise from the antenna. The simplest procedure is to resolve the unit antenna PC

* Communicated by the Author.

† $k = 188.5h_1I_1/\lambda d$.

into its two horizontal projection antennæ, namely, PA on the Y' axis equal to cos θ_2 and PB on the X' axis equal to sin θ_2. Applying the fields $\dot{E}_2$ and $\dot{E}_3$, respectively, to the two projection antennæ, we find that the resultant voltages are

$$E_2 = \dot{E}_2 \cos \theta_2 \tag{25}$$

and

$$E_3 = \dot{E}_3 \sin \theta_2 \tag{26}$$

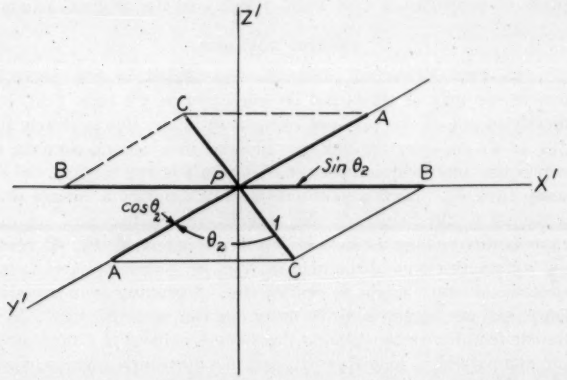
while the total voltage

$$E = \dot{E}_2 \cos \theta_2 + \dot{E}_3 \sin \theta_2, \tag{27}$$

E_1 being zero.

If our antenna is inclined to the horizontal plane by the

FIG. 11.



angle α_2 measured upward, as shown in Fig. 12, then we must proceed in a similar manner to resolve it into its three projection antennæ; the vertical projection antenna on the Z' axis will obviously have a relative value PD or sin α_2, while the horizontal projection antennæ PA will now have a value cos α_2 cos θ_2, and PB the value cos α_2 sin θ_2 (see also p. 418). The resultant induced voltages will now be

$$E_1 = \dot{E}_1 \sin \alpha_2, \tag{28}$$

$$E_2 = \dot{E}_2 \cos \alpha_2 \cos \theta_2, \tag{29}$$

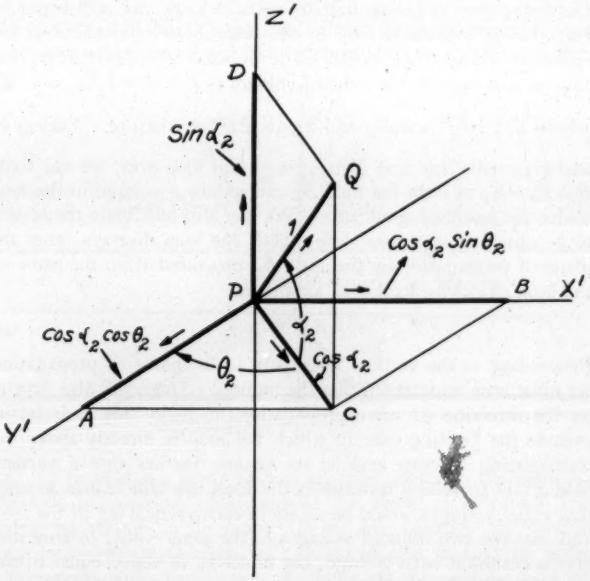
$$E_3 = \dot{E}_3 \cos \alpha_2 \sin \theta_2, \tag{30}$$

while the total voltage is

$$E = \dot{E}_1 \sin \alpha_2 + \dot{E}_2 \cos \alpha_2 \cos \theta_2 + \dot{E}_3 \cos \alpha_2 \sin \theta_2 . \qquad (31)$$

The final step in the voltage determination consists now of obtaining the values of the three component fields $\dot{E}_1$, $\dot{E}_2$, and $\dot{E}_3$

FIG. 12.



from the table on page 426, applying the same to equation (31) and obtaining the algebraic sum; due regard being given to the signs of the component fields as well as of the functions of the angles α_2 and θ_2. As an example, let us consider the case of the vertical loop transmitter; we obtain the values of the component fields from the table on page 426, and in this case reverse the signs so as to obtain a positive vertical field, we then have

$$\dot{E}_1 = \cos \beta \cos \theta_1 ; \; \dot{E}_2 = - \sin \beta \cos \theta_1 ; \; \dot{E}_3 = - \sin \beta \sin \theta_1$$

substituting in equation 31, simplifying and rearranging we obtain

$$E = \sin \alpha_2 \cos \beta \cos \theta_1 - \cos \alpha_2 \sin \beta \cos (\theta_1 - \theta_2) . \qquad (32)$$

(2) *The Vertical Receiving Loop.*—Having found and applied the general equation for an inclined receiver, we will now proceed to the slightly more involved equations for loops. Confining our attention first to vertical loops, we will begin by considering a vertical loop in the same horizontal plane as the transmitter and lying in the plane of wave propagation; in that case we can express the induced voltage as $E = E_1 - k_1 k \dot{E}_1 - k_1 \mathfrak{E}$, where k_1‡ is $\frac{2\pi l_2}{\lambda} \times h_2 N_2$ and k‡ is $\mathfrak{E}/\dot{E}_1$ as before. Taking k_1 and k as unity for unit distance and unit loop area, we can write $E = E_1 - \dot{E}_1$ as only the field $\dot{E}_1$ can induce a voltage in the loop under the assumed conditions. We can also anticipate the results to be obtained later and state that if the loop diverges from the plane of propagation by the angle θ_2, measured from the plane of the loop clockwise to the Y' axis, that

$$E = E_1 = \dot{E}_1 \cos \theta_2 . \qquad (33)$$

Proceeding to the vertical loop lying in the plane of propagation we must now understand that the induced voltage will also depend on the direction of wave propagation; to make this clear let us assume the limiting case in which the loop is directly above the transmitting antenna and let us assume further that a vertical field $\dot{E}_1$ is travelling upward to the loop, we will realize at once that equal voltages would be set up in each vertical leg of the loop and that the two induced voltages in the same would balance and give a resultant zero voltage; the effect is, in short, equal to the projection of the field $\dot{E}_1$ on the wave front or the resultant potential gradient acting on the loop as shown in Fig. 13; expressed geometrically this effective value is $\dot{E}_1 \cos \beta$; we can therefore write

$$E_1 = \dot{E}_1 \cos \beta . \qquad (34)$$

We know that no voltage is induced in the vertical loop in question by field $\dot{E}_2$ or $\dot{E}_3$ when the loop is in the same horizontal plane as the transmitter, or, in other words, when the angle of

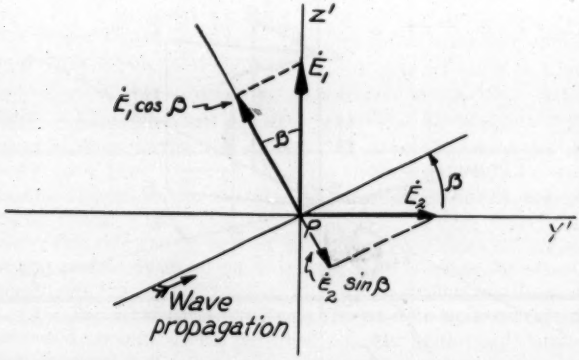
‡ $k_1 k = 1185 A_2 h_1 N_2 I_1 / \lambda^2 d$.

elevation β is zero; if, however, the elevation is not zero but 90 degrees, we will at once realize that the field $\dot{E}_2$ will induce a voltage E_2 in our loop and that at any angle less than 90° a voltage proportional to the projection of $\dot{E}_2$ on the wave front will result so that we can write

$$E_3 = -\dot{E}_2 \sin \beta \qquad (35)$$

it being noted in Fig. 13 that the voltage produced by a positive $\dot{E}_2$ is opposed to the voltage induced by a positive $\dot{E}_1$ (see also Fig.

FIG. 13.



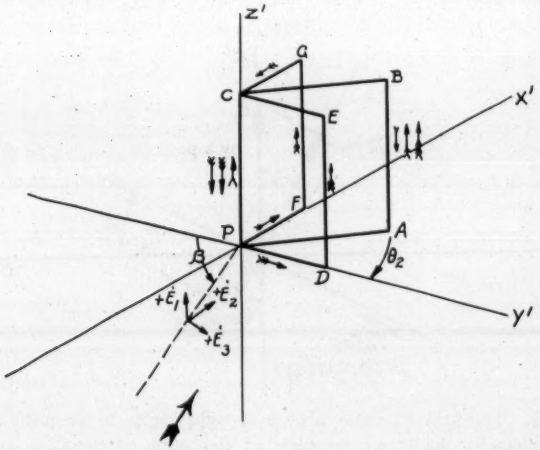
14). The field $\dot{E}_3$, being always at right angles to the plane of the loop in question, regardless of the angle of elevation, can induce no voltage in the same. If we now consider the vertical loop to be turned through 90° anti-clockwise so that its plane corresponds with the X' axis, we find that the vertical field $\dot{E}_1$ will induce no voltage under any condition, as any voltages induced in the vertical sides of the loop will balance one another, thus giving a zero resultant. The field $\dot{E}_2$ will induce no voltage in the loop, as it is always at right angles to the plane of the loop. The field E_3 will induce a maximum voltage E_3 when the loop is directly above the transmitter as this field will then have the maximum effect on the loop in question. At angles less than 90° the effect of this field will be proportional to the projection of the loop on the plane of propagation or to sin β, and as the

induced voltage due to a positive $\dot{E}_3$ is again opposed in direction to that induced by a positive $\dot{E}_1$ (Fig. 14), we must write

$$E_2 = -\dot{E}_3 \sin \beta . \tag{36}$$

Let us now assume that our vertical loop lies at an angle θ_2 to the Y' axis, the angle being again measured clockwise from the plane of the loop to the Y' axis as in Fig. 14; our unit loop

FIG. 14.



PABC can now be resolved into two projection loops in the same manner as was done in the case of antennæ. We must therefore consider the projection loop corresponding with the Y' axis or *PDEC*, whose relative value is $\cos \theta_2$, and the second projection loop on the X' axis or *PFGC*, whose relative value is $\sin \theta_2$. Applying our formulæ for vertical loops in the plane of Y' to our projection loop *PDEC*, we have from equation 34

$$E_1 = \dot{E}_1 \cos \beta \cos \theta_2 , \tag{37}$$

which resolves into equation (33) when β is zero. From equation 35 we have similarly

$$E_2 = -\dot{E}_2 \sin \beta \cos \theta_2 . \tag{38}$$

By applying equation 36 for loops in the plane of X' to our loop $PFGC$, we obtain

$$E_3 = -\dot{E}_3 \sin\beta \sin\theta_2 . \qquad (39)\S$$

Our resultant voltage for the special case of a vertical loop is therefore

$$E = E_1 + E_2 + E_3 = \dot{E}_1 \cos\beta \cos\theta_2 - \dot{E}_2 \sin\beta \cos\theta_2 - \dot{E}_3 \sin\beta \sin\theta_2 . \quad (40)$$

Let us now apply this equation to the specific case of reception from a transmitting antenna inclined above the horizontal by the angle α_1. The values of $\dot{E}_1$, $\dot{E}_2$, and $\dot{E}_3$ are obtained from equations 9, 10 and 11, pages 418 and 419, or from the table on page 426; if we insert the same in their proper places and with their proper signs in equations (40), we obtain after rearranging and simplification the following:

$$E = \sin\alpha_1 \cos\beta \cos\theta_2 - \cos\alpha_1 \sin\beta \cos(\theta_1 - \theta_2) , \qquad (41)$$

which corresponds with equation (32) for the reversed case, except with regard to the suffixes. It is evident, therefore, as might have been expected, that the relationship between two antennæ is fixed (under the present general assumptions), regardless of which is the transmitter or receiver. In the table given below, this rule can be applied in case the conditions of interest are the reverse of those listed, it being only necessary to reverse the suffixes.

(3) *The Horizontal Receiving Loop.*—We have so far not concerned ourselves with the third possible basic loop, namely, the horizontal loop; this loop is, however, not affected by the vertical field $\dot{E}_1$ nor the horizontal field $\dot{E}_2$, as the former induces no voltages in the loops' sides while the voltages induced by the latter balance out and produce a zero loop potential. The $\dot{E}_3$ field induces a maximum voltage E_3 at zero elevation and zero voltage at 90°; in short, the voltage induced is proportional to the projection of the loop on the plane of propagation or to $\cos\beta$, we can, therefore, write

$$E = E_3 = -\dot{E}_3 \cos\beta . \qquad (42)$$

(See also equations 19 and 20, page 421.)

(4) *The Inclined Receiving Loop.*—We obtain from the above, the final general equation for an inclined loop in which the angle of inclination, which we call δ_2, is measured as shown in

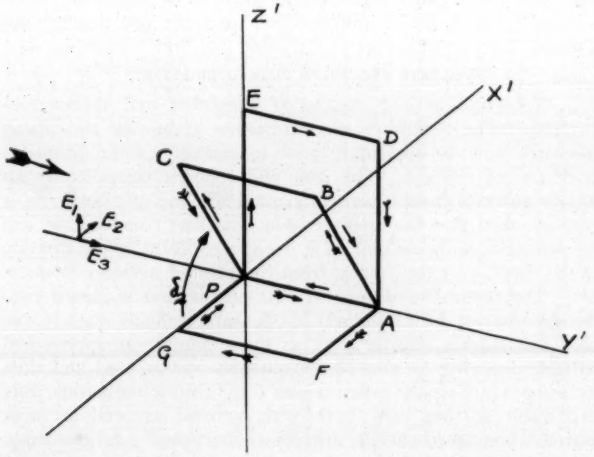
§ See equations 13, 14, 15, page 421.

Chart of Induced Voltage Factor Equations.

	Transmitting Antenna.	Receiving Antenna.	Induced Voltage Factor $E = E_1 + E_2 + E_3$.
I	*VA*	*IA*	$\cos\beta\,(\sin\alpha_2\cos\beta - \cos\alpha_2\sin\beta\cos\theta_2)$ (Eq. 46)
II	*HA*	*IA*	$\sin\beta\cos\theta_1\,(\cos\alpha_2\sin\beta\cos\theta_2 - \sin\alpha_2\cos\beta) + \cos\alpha_2\sin\theta_1\sin\theta_2$
III	*IA*	*IA*	$\sin\alpha_1\sin\alpha_2 + \cos\alpha_1\cos\alpha_2\cos(\theta_1-\theta_2) - (\sin\alpha_1\sin\beta + \cos\alpha_1\cos\beta\cos\theta_1)(\sin\alpha_2\sin\beta + \cos\alpha_2\cos\beta\cos\theta_2)$
IV	*HA*	*VA*	$\sin\beta\cos\beta\cos\theta_1$
V	*VA*	*VA*	$\cos^2\beta$
VI	*HA*	*HA*	$\cos(\theta_1-\theta_2) - \cos^2\beta\cos\theta_1\cos\theta_2$
VII	*VL*	*IL*	$\cos\theta_1\cos\theta_2\sin\delta_2 + \sin\beta\sin\theta_1\,(\sin\beta\sin\theta_2\sin\delta_2 + \cos\beta\cos\delta_2)$
IIX	*HL*	*IL*	$\cos\beta\,(\sin\beta\sin\theta_2\sin\delta_2 + \cos\beta\cos\delta_2)$
IX	*IL*	*IL*	$\cos\theta_1\cos\theta_2\sin\delta_1\sin\delta_2 + (\sin\beta\sin\theta_1\sin\delta_1 + \cos\beta\cos\delta_1)(\sin\beta\sin\theta_2\sin\delta_2 + \cos\beta\cos\delta_2)$
X	*HL*	*VL*	$\cos\beta\sin\beta\sin\theta_2$
XI	*VL*	*VL*	$\cos(\theta_1-\theta_2) - \cos^2\beta\sin\theta_1\sin\theta_2$
XII	*VA*	*IL*	$\sin\delta_2\cos\beta\cos\theta_2$
XIII	*HA*	*IL*	$\sin\delta_2\sin\beta\cos(\theta_1-\theta_2) + \cos\beta\cos\delta_2\sin\theta_1$
XIV	*IA*	*IL*	$\sin\delta_2\,(\cos\alpha_1\sin\beta\cos\theta_1\cos\theta_2 - \sin\alpha_1\cos\beta\cos\theta_2) + \cos\alpha_1\sin\theta_1\,(\sin\beta\sin\theta_2\sin\delta_2 + \cos\beta\cos\delta_2)$
XV	*VA*	*VL*	$\cos\beta\cos\theta_2$
XVI	*HA*	*VL*	$\sin\beta\cos(\theta_1-\theta_2)$
XVII	*IA*	*VL*	$\cos\alpha_1\sin\beta\cos(\theta_1-\theta_2) - \sin\alpha_1\cos\beta\cos\theta_2$ (Eq. 41)
XIIX	*VA*	*HL*	0
XIX	*HA*	*HL*	$\sin\theta_1\cos\beta$
XX	*IA*	*HL*	$\cos\alpha_1\cos\beta\sin\theta_1$

Fig. 15, so that a positive field $\dot{E}_3$ will induce a voltage opposing the voltage induced by a positive field $\dot{E}_1$. The inclined loop *PABC* must first be resolved into two projection component loops, a horizontal projection loop *PAFG* whose relative value is cos δ_2 and a vertical projection loop *PADE* whose relative value is sin δ_2. The vertical projection loop may or may not correspond with the Y' axis, if it differs from the same by the

FIG. 15.



angle θ_2 then it must in turn be resolved into a vertical projection loop corresponding with the Y' axis and one corresponding with the X' axis. In this manner we arrive at the two final vertical projection loops whose relative values are now cos θ_2 sin δ_2 in the Y' axis and sin θ_2 sin δ_2 in the X' axis. Applying equation 40 to the two vertical projection loops and adding the same to equation 42 applied to the horizontal projection loops, we obtain the final general equation for any loop:

$$E = E_1 + E_2 + E_3 = \dot{E}_1 \cos\beta \cos\theta_2 \sin\delta_2 - \dot{E}_2 \sin\beta \cos\theta_2 \sin\delta_2 - \dot{E}_3 (\sin\beta \sin\theta_2 \sin\delta_2 + \cos\beta \cos\delta_2) . \quad (43)\|$$

|| Compare reception components of (43) with equations 21, 22, and 23 page 422.

From the general equations 31 and 43 we can, in turn, develop specific induced voltage equations for any of the transmitters listed in the chart of page 426 by inserting the values of the component fields in the two basic equations in question, modified in turn for vertical and horizontal loops and antennæ by the use of proper values of α and δ. We have in the chart (p. 296) chosen the relative signs of the component fields in such a manner that the resultant voltage formulæ will be positive, it being noted that the negative signs are of importance only when fields to be added and due to different antennæ are 180 degrees out of phase.

VOLTAGE RECEPTION CHARACTERISTICS.

1. *Reception as a Function of Elevation and Distance.*—$E = f(\beta)$. The reception characteristics given in the above chart will now be applied in part to certain specific problems which are of interest. The first will concern reception by an airplane antenna from a vertical ground antenna or *vice versa*, it being assumed that the airplane, which acts as counterpoise and thus replaces one dipole unit, is flying at a constant height directly toward, over, and then away from the ground antenna in question. The reason for discussing this case is that it caused considerable interest during the war at our training fields when it was noted that signals became weak as the antenna was approached in flight, dropping to zero as the antenna was crossed and then increasing again as the antenna was left behind; numerous tests were made at that time both with vertical as well as with umbrella antennæ of various degrees of sharpness. A little study at once indicated that the effect was due to the fact that the field directly over such an antenna is zero, further that the reception factor of the receiving antenna is also zero along its effective axis, which corresponds closely with the upper third of the trailing airplane antenna. A study of the first equation of our chart of induced voltage factors will make clear what actually takes place. This equation must first be simplified, as θ_2 is actually 0, β being taken as increasing from 0° to 180°.¶ A further modification is required as the distance between the antennæ varies and is not now unity. If we assume the airplane to be at unit altitude then we can express the actual distance as

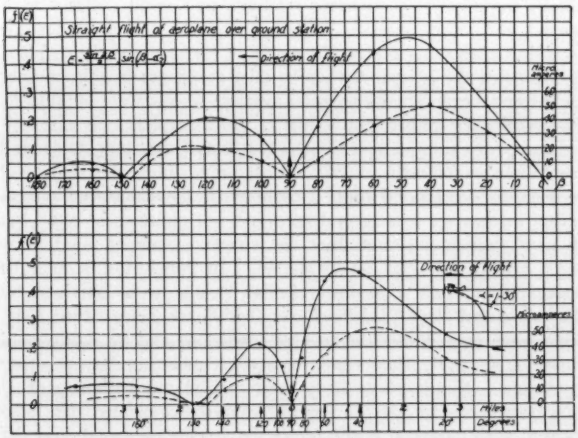
¶ If β were limited between 0 and 90° then θ_2 would change to 180° on departure.

$1/\sin\beta$, we can therefore show the resultant induced voltage as $E = f(\sin\beta)$ (E is inversely proportional to the distance). We now find that the equation for E simplifies to:

$$E = \sin\beta\cos\beta\sin(\beta - \alpha_2) = \frac{\sin 2\beta}{2}\sin(\beta - \alpha_2). \qquad (44)$$

Let us take a specific case as an example in which we will choose an antenna angle of $-30°$, the calculated values of $f(E)$ for

FIG. 16.



every twenty degrees of β are given in the table below as well as the corresponding distances from the vertical antenna; the height of the airplane being taken as one mile. Fig. 16 gives these data graphically, it being noted that negative values are also shown above the zero line.

β	0	20	40	60	80	90	100	120	140	150	160	180°
$f(E)$	0	.247	.465	.433	.162	0	.132	.216	.086	0	−.056	0
d	∞	2.75	1.2	.58	.18	0	.18	.58	1.2	1.73	2.75	∞
Microampere	—	32	51	34	12	0	11	21	10	2	6	—

The qualitative data obtained during the first observations were later supplemented by actual measurements capable of quantitative conversion and obtained in the following manner: An air-

plane was flown over a straight course over the ground receiving antenna, a constant current being maintained in the airplane antenna during the entire flight of about six miles, the air speed of the plane and the altitude were kept as constant as possible and the antenna length was so adjusted that the upper part of the same hung at practically 30 degrees below the horizontal. At the receiving station there was in use a simple tube receiver with a microammeter in the last stage, the plate current of the latter being controlled by an adjustable negative grid bias so as to obtain comparatively accurate readings and good deflections, a second and third observer with a theodolite set up under the receiving antenna observed the angle of elevation of the airplane and notified the operator when to take readings; in this manner and after several repetitions good average results were obtainable. The results for an airplane flying at approximately one mile altitude are, for example, given in the last line of the above table, and are shown graphically in Fig. 16 as dotted lines, the same will be seen to correspond quite closely with the calculated curves except in that the true second zero was not obtained at 150° but at 145°, which indicated that the effective antenna angle was −35° instead of −30° as estimated. In conclusion it will be interesting to note that very similar results were obtained by Buchwald and Hase (*Jahrbuch der Drahtlosen Telegraphie,* Feb., 1920, page 109) under the reverse conditions and by Baldus and Hase (*J. d. D. T.,* May, 1920, page 369) under similar operating conditions. Similar tests have been carried out with a vertical loop transmitter at Dayton; in this case the calculated data also checked with observed results; here the voltage or signal does not become zero directly over the loop but is very nearly a maximum, the true maximum ** being found at an elevation of 75° for a thirty-degree antenna, while a true zero is again found at 150°, as would be expected and as would be obtained from the corresponding equation

$$E = \sin \beta \sin (\beta - \alpha_2). \qquad (45)$$

2. *Reception as a Function of the Airplane Antenna Direction.* —$E = f(\theta)$. The second case of interest is the directional effect of the airplane antenna, either as a receiver or transmitter; this was also noted early in airplane radio operation and was of such

** By differentiating E with respect to β in (45) and equating to zero, we find that maxima occur when $\tan 2\beta = \tan \alpha_2$.

importance with low-power radio sets that special instructions were necessary in artillery observation work, so that the airplane would be flown in the proper direction when operating the transmitter; that is, toward the receiving or ground station in order to obtain the best results. It was considered important to obtain some definite characteristics and this was done first very qualitatively by noting variations of signal strength for different airplane positions and later quantitatively by the following general method which consisted of picking out a reference point on the ground, then flying over this point in various directions; a signal was sent while crossing over the point in question while the receiving station operator made note of the deflections obtained on a microammeter for various positions of the airplane, as in the previous case. These results checked very closely with those obtained theoretically. The equation of immediate interest is the first equation of the induced voltage factor chart for a vertical ground antenna and an inclined airplane antenna; in this equation the elevation and antenna angle are taken as constant, while θ_1 is variable, it being assumed that the airplane is transmitting so that the suffixes must be 1; we can say therefore that $E = f(\theta_1)$; there are now three conditions of operation, namely, if the angle β is greater than α_1, equal to α_1, or less than α_1; we will assume β to be 45°, although this is of course excessive, β would actually be determined by the artillery range and the altitude of the airplane, being generally less than 20°. Let us consider various airplane antennæ, assuming that α_1 is $-30°$ in the first case, $-45°$ in the second, and $-60°$ in the third (similarly we could assume the antenna to be constant while the elevation was varied above and below 45°, either by assuming the airplane to be over the target at various heights, or by assuming the target to be further away or nearer to the artillery). Calculations from formula

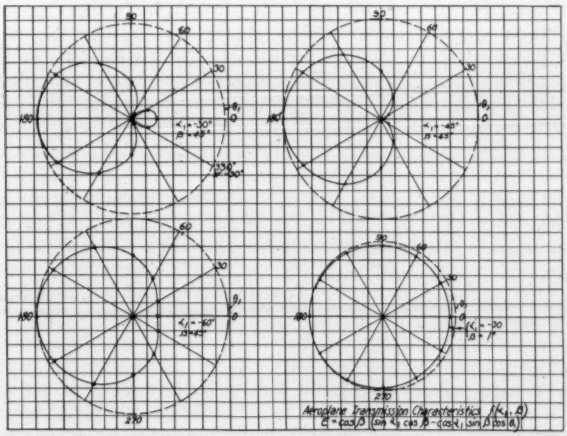
$$E = \cos\beta\,(\sin\alpha_1\cos\beta - \cos\alpha_1\sin\beta\cos\theta_1)\,, \qquad (46)$$

give the following results, shown graphically in Fig. 17:

θ_1.	$\alpha_1 = -30°$.	$\alpha_1 = -45°$.	$\alpha_1 = -60°$.	$\alpha_1 = -30°$ and $\beta = 1°$.
0	.685	.707	.684	.515
30	.626	.660	.650	.513
60	.467	.531	.559	.507
90	.250	.353	.434	.500
120	.033	.177	.309	.493
150	−.126	.048	.218	.487
180	−.185	.000	.184	.485

Obviously, therefore, if β is fixed, then the more nearly vertical the airplane antenna is, the less directional will the results be; on the other hand, β should be considerably less than α_1. This accounts for the fact that directional effects are less noticeable the further the airplane is from the ground station or the lower the altitude at which the airplane is flying. The directional effect becomes rapidly more noticeable as the operating range is decreased below twenty miles; in short, the effect is not entirely due to the antenna angle as is frequently supposed, but to a great

FIG. 17.



extent to the angle of elevation; in other words, to the height and distance of the airplane. For this reason let us consider a case in which a bombing plane is assumed to be flying at an altitude of five miles and at a distance of 300 miles from its home station, neglecting the curvature of the earth the angle β is found to be approximately $1°$; suppose further that the $-30°$ antenna is in use, an antenna which would normally be considered to be poor and highly directional, then by calculation we find the values shown in the last column of the above table, the distance being assumed to be unity, as we are not here interested in the reduction of intensity due to distance. Fig. 17 shows the results which will be seen to be practically non-directional. Practical tests have been

made on numerous occasions, notable among which were tests in which the airplane was listened to directly by a station located three miles away and simultaneously but indirectly through the rebroadcasting station WLW at Cincinnati, fifty miles away; in this test the direct signals from the airplane, which was circling at 1000 feet, varied greatly in intensity while the rebroadcast signals were not noticed to vary at all; this being, of course, due to the fact that the angle β from the direct reception point was about 40°, while the angle β from the distant and rebroadcasting point to the airplane was approximately .3° or 18′. The objection to directional airplane antennæ is theoretically not so much due to intensity, variations as functions of θ_1, but rather due to the decrease in field intensity and consequently in signal strength with a decrease of the antenna angle; this is, of course, more than overcome in general by the fact that a vertical antenna of more than a few feet height cannot well be obtained on an airplane, while inclined antennæ of 150- to 300-foot length are in general use. Just as the voltage reception characteristic can be obtained for a definite airplane antenna and ground station, so can we also obtain the characteristics between two airplanes flying in different relative positions in space. If both airplanes are equipped with similar trailing antennæ, it is only necessary to make use of the third formula of our chart for two inclined antennæ and to apply simplifying assumptions; namely, that the antennæ of the two planes are equal ($\alpha_1 = \alpha_2$) and that the two airplanes are flying along parallel routes ($\theta_1 = \theta_2$); our formula then simplifies to the following:

$$E = 1 - (\sin\alpha \sin\beta + \cos\alpha \cos\beta \cos\theta)^2; \qquad (47)$$

if we now make the further specific assumptions, namely, that $\alpha = -30°$ and that $\beta = 10°$ in one case and 60° in the second, then from the above equation we obtain the following table and the graphical results shown in Fig. 18:

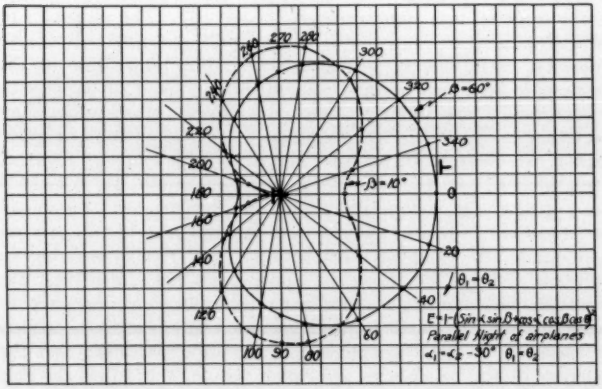
θ	0	20	40	60	80	90	100	120	140	160	180	
E	.41	.485	.678	.883	.996	.993	.947	.744	.465	.22	.13	(when β is 10°)
E	1	.999	.989	.953	.872	.813	.743	.58	.42	.30	.25	(when β is 60°).

This will give a general idea as to how the voltage reception characteristics vary, especially when β is small, in which case it is seen that the best results are obtained when the airplanes are flying nearly side by side.††

†† For a given β and α the position for maximum E is obtained by differentiating E with respect to θ in (47) and equating to 0: $\tan 2\beta = \dfrac{\cdot 2 \cos\theta \tan\alpha}{\cos^2\theta - \tan^2\alpha}$.

3. *Reception in Circular Flight and Resultant Bearing Errors.*—The following is a most important case, as will be seen immediately, not only because it applies directly to the location of aircraft by means of loop receivers as well as to guiding aircraft by loops or other directional transmitters, but also because certain bearing errors are met with in actual tests which can be mathematically calculated with considerable precision. Although

FIG. 18.



various types of directional receivers or transmitters can and have been employed, we will consider here only the loop and horizontal antenna, while the airplane antenna will be taken to be inclined below the horizontal by the angle $-\alpha_2$. We must begin with the use of equation XVII of our chart with the proper suffixes. Let us consider the airplane in circular flight in a clockwise direction around the ground station so that θ_2 ‡‡ is 90°, then our basic equation becomes

$$E = \cos \alpha_2 \sin \beta \sin \theta_1 - \sin \alpha_2 \cos \beta \cos \theta_1 \qquad (48)$$

for the loop, and from equation II

$$E = -\sin \alpha_2 \sin \beta \cos \beta \cos \theta_1 + \cos \alpha_2 \sin \theta_1 \qquad (49)$$

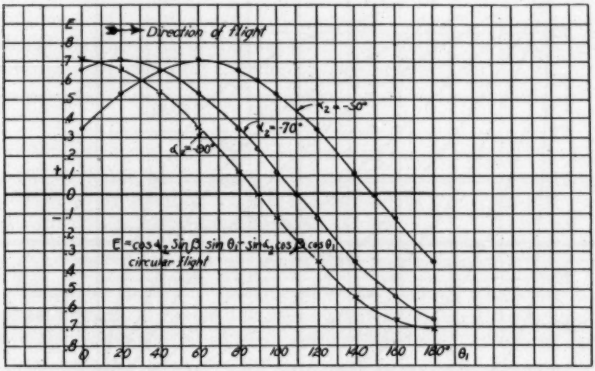
‡‡ θ_2 is measured clockwise from the horizontal projection of the antenna to the Y' axis!

for the horizontal antenna. Let us assume β to be 45° and then calculate E for various α_2 in equation 48; this gives us the values in the table below, shown graphically in Fig. 19.

θ_1	0	20	40	60	80	90	100	120	140	160	180	
E	.35	.54	.66	.71	.66	.61	.54	.35	.12	−.12	−.35	when α_2 is −30°
E	.66	.71	.66	.54	.35	.24	.12	−.12	−.35	−.54	−.66	when α_2 is −70°
E	.71	.66	.54	.35	.12	0	−.12	−.35	−.54	−.66	−.71	when α_2 is −90°

It is evident that our maxima and minima have been shifted in the direction of travel by 20 degrees in the case of the 70° antenna and by 60° in the case of the 30° antenna. As such shifts actually occur and have been found by direct observation

FIG. 19.



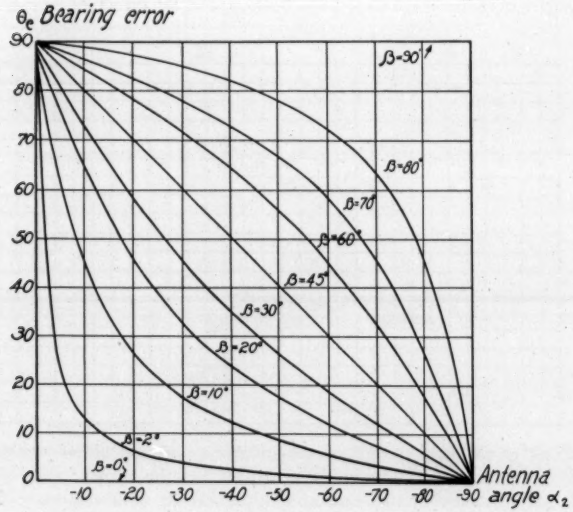
to agree within the error of measurement with calculated values, it is of interest to obtain the equation for the errors; this can be done readily by differentiating equation 48 with respect to θ_1 and equating to 0; in this manner we obtain

$$\tan\theta_1 \tan\theta_e = -\tan\beta/\tan\alpha_2. \qquad (50)$$

The formula indicates that the bearing angle θ_e for the maximum signal is the true bearing of the point in the horizontal plane of the loop at which the antenna, if continued at the angle α_2, would cut the plane in question, and that the error is zero when β is zero. Fig. 20 gives the errors obtained in true circular flight for various antennæ and at different elevations; from this chart or

from equation 48 we see also that the error is zero if the angle θ_1 is 0 or 180, or if the antenna is vertical. It is clear, therefore, that if an airplane has an inclined antenna and is receiving from a loop or alternately from two loops as is done in equisignal radio beacon operation, that the bearing obtained will only be correct when the airplane is flying toward or away from the beacon station; similarly, if the bearing of an airplane is being obtained by a compass station or ground receiving loop, that the same will

FIG. 20.



only be correct under like conditions; it is quite obvious therefore that large errors may be met with in spotting, if bearings are obtained by several direction finding stations, the errors being greater the larger β, the smaller α_2, and the nearer θ_2 is to 90° or 270°. It will be interesting here to quote the specific results obtained in a certain test in which the airplane was flown at a distance of 26.7 km. from the station, at right angles to the line of sight and at various altitudes. The equisignal method was used

for obtaining the bearing from a ground transmitting loop and the errors were expressed in kilometres from the true bearing.

Altitude.	Calculated Bearing Error.	Measured Bearing Error (ave.)
1510 m.	9.8 km.	10.2 km.
1230	8	9.1
910	6	5.3
610	4	2.8
310	2	1.6
150	1	1.5

The difference between the calculated and measured errors is easily understood when it is remembered that the altitude of the airplane, the exact point of signal balance, and the air speed (of which the antenna angle is a function) are difficult to determine or to maintain with any great accuracy. If the transmitting antenna should be a horizontal dipole the error can readily be found by differentiating equation 49; we obtain thus

$$\tan \theta_1 = \tan \theta_e = \frac{-\cot \alpha_2}{\cos \beta \sin \beta}. \tag{51}$$

It is interesting to note that if we obtain the bearing errors by the two methods, assuming right angle flight, we find by dividing equation 50 by equation 51 that the quotient is $\sin^2 \beta$, so that we have a means of obtaining the angle of elevation.

THE SUMMATION OF FIELDS DIFFERING IN PHASE.

There are numerous combinations of antennæ which are of interest but only a few will be considered here. First, let us consider the combination of two vertical antennæ. We will, as before, consider even current distribution in each antenna but must introduce a new symbol ϕ_s, which represents the space phase displacement and which is generally expressed as:

$$\phi_s = \frac{2\pi l \cos \theta_1}{\lambda} \tag{52}$$

where l is the horizontal distance between the two antennæ; as a matter of fact, this is the equation in the horizontal plane. The equation for the field in space can be readily shown to be

$$\phi_s = 2\pi l \cos \beta \cos \theta_1 / \lambda. \tag{53}$$

(See Fig. 21.) If the currents in the two antennæ are not in phase but have a definite phase relationship, then we must also consider the current phase displacement which we will designate

by ϕ_c; if the two currents are equal and in phase, the value of ϕ_c is 0, and if the two currents are in opposition then ϕ_c is 180°. The resultant of two fields is

$$\dot{E}_r = \sqrt{\dot{E}^2 + \dot{E}^2 \cos(\phi_s + \phi_c)} = \dot{E}\sqrt{2(1 + \cos(\phi_s + \phi_c))} = 2\dot{E}\cos\frac{\phi_s + \phi_c}{2}. \quad (54)$$

If ϕ_c is 0 then $\dot{E}_r = 2\dot{E}\cos(\phi_s/2)$, while if ϕ_c is 180°, $\dot{E}_r = -2\dot{E} \times \sin(\phi_s/2)$. The latter can, if ϕ_s is small, be written

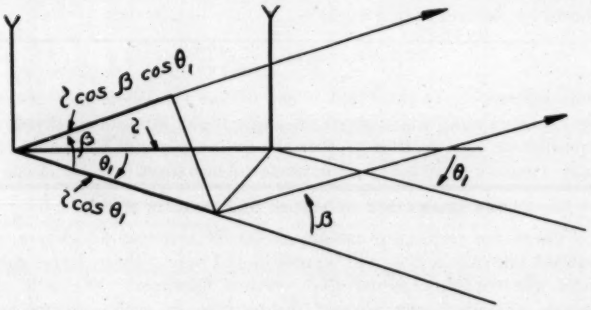
$$\dot{E}_r = -\dot{E}\phi_s = -\dot{E}2\pi l \cos\beta \cos\theta_1/\lambda \quad (55)$$

and if the antenna current is not unity but say $\lambda/2\pi l$ then

$$\dot{E}_r = -\dot{E}\cos\beta\cos\theta_1. \quad (56)$$

In exactly the same manner we can evolve the equation for a

FIG. 21.



doublet or pair of horizontal antennæ lying vertically above one another, here $\dot{E}_r = 2\dot{E}\cos\frac{\phi_s + \phi_c}{2}$, where $\phi_s = 2\pi h \sin\beta/\lambda$, h being the vertical height between the two units. If ϕ_c is again taken as 180°, we can write $\dot{E}_r = -2E\sin(\phi_s/2)$. If ϕ_s is small

$$\dot{E}_r = -\frac{\dot{E}2\pi h \sin\beta}{\lambda} \quad (57)$$

and if further the current is taken as $\lambda/2\pi h$, then

$$\dot{E}_r = -\dot{E}\sin\beta. \quad (58)$$

We can, of course, apply our various values of $\dot{E}_1$, $\dot{E}_2$, or $\dot{E}_3$ to these equations (56 and 58), and in this manner obtain the

resultant fields in space. As an example we will consider our two vertical antennæ with 180° current phase displacement. If we consider our distance l to be less than one-sixth of the wave-length, then the error made by replacing $\sin \phi_s$ by ϕ_s will be less than 1 per cent., and we can use equation 56; let us now proceed to apply our component fields for vertical antennæ§§ and we find immediately that $E_{r1} = -\cos^3 \beta \cos \theta_1$, $E_{r2} = \sin \beta \cos^2 \beta \cos \theta_1$ and $E_{r3} = 0$. If we follow the same steps for the horizontal doublet, assuming that h is also unity, then we obtain from equation 58: $E_{r1} = -\cos \beta \sin^2 \beta \cos \theta_1$, $E_{r2} = \sin^3 \beta \cos \theta_1$, $E_{r3} = \sin \beta \sin \theta_1$, adding these two groups together, respectively, we obtain $E_{r1} = -\cos \beta \cos \theta_1$, $E_{r2} = \sin \beta \cos \theta_1$, $E_{r3} = \sin \beta \sin \theta_1$, equations which we immediately recognize as those of a vertical loop. (See page 421, equations 13, 14, and 15.) We see, therefore, that by the proper use of our phase displacement and component field formulæ, we can readily obtain the resultant field equations for antenna groups, from which we can in turn obtain the voltage factor equations in the usual manner.

As a final example we will consider the very simple case of two horizontal loops placed vertically above one another by the distance h and in which equal currents, 180° out of phase from one another, are flowing. Our basic formulæ for field intensities of a horizontal loop (426) show us that $\dot{E}_1 = \dot{E}_2 = 0$ and that $\dot{E}_3 = \dot{E} = \cos \beta$; on the other hand, and considering the two loops, we can state that $\phi_s = \frac{2\pi h \sin \beta}{\lambda}$ and $\phi_c = 180°$. The general equation is

$$\dot{E}_r = 2\dot{E} \cos \left\{ \frac{\pi h \sin \beta}{\lambda} + \frac{\phi_c}{2} \right\};$$

this simplifies to

$$\dot{E}_r = -2 \cos \beta \sin \left\{ \frac{\pi h \sin \beta}{\lambda} \right\}; \tag{59}$$

and if h/λ is small then

$$\dot{E}_r = -2 \cos \beta \left\{ \frac{\pi h \sin \beta}{\lambda} \right\}. \tag{60}$$

In the following table, values of $\dot{E}_r$ are given as functions of the

§§ See chart, p. 426, for *VA* and *HA*. Make $\dot{E}_1$ positive, $\dot{E}_2$ and $\dot{E}_3$ negative in each case!

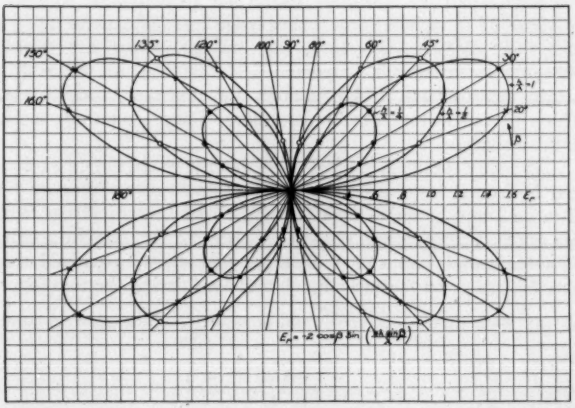
elevation and for different ratios of h/λ, the data being also given graphically in Fig. 22:

Parallel Horizontal Loops.

β	0	20	30	45	60	80	90	h/λ	Equation.
$\dot{E}_r$	0	.50	.67	.78	.67	.27	0	1/4	(60)
	0	.49	.66	.76	.64	.24	0	1/4	(59)
	0.	.96	1.24	1.28	.98	.34	0	1/2	(59)
	0	1.64	1.74	1.12	.41	.02	0	1	(59)

The effect of the above loop combination on an inclined air-

FIG. 22.



plane antenna can be readily determined from equation 30 by inserting the field value of equation 60, it being remembered that the fields $\dot{E}_1$ and $\dot{E}_2$ are zero, we therefore have $E = -2 \cos \beta \times \left(\frac{\pi h \sin \beta}{\lambda}\right) \cos \alpha_2 \sin \theta_2$, which in turn simplifies to $E = -\cos \beta \sin \beta \times \cos \alpha_2 \sin \theta_2$ when the constant is made unity.

CONCLUDING RÉSUMÉ.

The present article deals with the reception characteristics of antennæ; the application of the previously obtained electrostatic field equations to receiving antennæ, by which means, induced

voltage equations are evolved; the directional effects obtained between airplanes and ground stations as well as between airplanes in parallel flight; and the bearing errors met with when using loop or horizontal antennæ. It is shown that the transmission and reception characteristics of a given antenna, complying with our basic assumptions, are equal and that the induced voltage characteristics obtained for two antennæ are the same regardless of which antenna is transmitting, it being only necessary to alter the suffixes as suffix 1 applies to transmitting antennæ and 2 to the receiving antennæ.

In conclusion the effect of antenna combinations, in which current and space phase displacements are taken into account, are discussed and equations including the phase displacement angles are evolved. By the application of these formulæ to straight antennæ combinations it is shown, for example, how the loop field equations can be readily evolved.

A Refinement of the Michelson-Morley Experiment. R. J. KENNEDY. (*Proc. Nat. Acad. Sciences,* Nov., 1926.)—The investigations here reported were made in order to examine the conclusions drawn by D. C. Miller from his repetitions of the famous Michelson-Morley experiment. "Professor Miller interprets his observations as indicating a motion of the sun through the ether with a velocity not less than 200 kilometres per second in a direction about right ascension 262 degrees, declination 65 degrees. He supposes that a contraction of the apparatus in the direction of motion occurs, which, however, departs from that given by the formula of Lorentz and Fitzgerald by an amount corresponding to a velocity of about 10 kilometres per second. That is, the average shift of the interference pattern, as an arm of his interferometer is turned through 90 degrees from the direction perpendicular or parallel to the direction of the inferred drift, is such as would be expected if the velocity of the apparatus were 10 kilometres per second and no contraction occurred." In order to get an observable shift of the interference pattern Professor Miller used a large interferometer with a light path 65 metres long. With an instrument of this size a shift corresponding to a velocity of 10 km./sec. could be produced by a change in the optical length of one path amounting to less than one part in a billion. The requisite alteration in optical length would be brought about by a difference in air pressure along the two arms of .002 mm. of mercury or by a difference of temperature of .001 degree.

In the present experiment the light paths were about 4 metres in length and the whole apparatus was sealed within a metallic case containing helium. "Because of its small size the apparatus could be effectively insulated, and circulation and variations in density in the

light paths nearly eliminated. Furthermore, since the value of $\mu - 1$ (μ = index of refraction) for helium is only about one-tenth that for air at the same pressure, it will be seen that the disturbing effects of changes in density of the gas correspond to those in air at only a tenth of an atmosphere of pressure." The apparatus was mounted on a slab of marble that floated in a pan of mercury. The light used was homogeneous and plane polarized, the electric vector lying in a horizontal plane. Two advantages accompanied the employment of polarized light. Certain rays that do not interfere are avoided and, again, the two rays that interfere can be made of just the same intensity.

"The experiment was performed in a constant-temperature room in the Norman Bridge Laboratory at various times of day, but oftenest at the time when Miller's conclusions require the greatest effect. The sensitiveness of the eye was rested for each trial by the placing or removal of a small weight on the slab before and after rotating it. As has been shown, a shift as small as one-fourth that corresponding to Miller's would be perceived. The result was perfectly definite. There was no sign of a shift depending on the orientation. Because an ether drift might conceivably depend on altitude, the experiment was repeated at the Mount Wilson Observatory, in the 100-inch telescope building. Here again the effect was null."

The importance of this experiment is that it confirms the results upon which the Theory of Relativity rests. Miller's investigation seemed to threaten the foundations of this important theory.

G. F. S.

Alleged Transmutation of Mercury into Gold.—H. HORTON SHELDON and ROGER S. ESTEY, of New York University (*Ind. and Eng. Chem.*, News Edition, 1926, **4**, No. 23, 5–7), have repeated the experiments of European investigators who reported the production of minute amounts of gold from mercury by transmutation in the mercury arc. Sheldon and Estey used three types of lamp, two designed by themselves, and one of European design and manufacture. After the mercury arc had been maintained for periods as long as 171 hours 50 minutes, the mercury in the lamp and the deposits on its walls were subjected to a thorough examination for the presence of gold. However, the presence of gold was never detected. Therefore the transmutation had not occurred.

J. S. H.

Preparation of Oxygen by Enzyme Action.—H. L. WIKOFF and J. B. BROWN, of Ohio State University (*Jour. Chem. Education*, 1926, **3**, 1434–1435), recommend that oxygen be prepared on a laboratory scale by mixing hydrogen peroxide with an aqueous emulsion of yeast, prepared from compressed yeast. The enzyme catalase, which occurs in yeast, functions as a catalyst and decomposes the hydrogen peroxide with the formation of water and oxygen.

J. S. H.

THE MOVEMENTS OF FLUIDS IN POROUS SOLIDS.

BY

P. G. NUTTING, Ph.D.

Geophysicist, U. S. Geological Survey;
Member of the Institute.

THE movements of ground waters and petroleum through sand and rock, the wetting of soils, the penetration of building material by water and the numerous other practical problems involve a knowledge of the behavior of fluids in porous solids. Theoretical physics has supplied laws of motion applicable to uniform channels of simple form; the cylindrical tube, the open trough and the channel bounded by parallel walls. In many important problems, however, the ducts are not of uniform section and calculations of movements are of little value.

In many special cases only the *effective* pore section in a particular direction is of practical interest. This may be readily determined by simple laboratory tests described below. When this is known, movements under specific heads, pressures or capillary forces may be calculated without difficulty.

By the ordinary law of flow, applicable to fluids possessing simple viscosity, the longitudinal force f per unit area of surface s is proportional to the velocity gradient du/dz produced by it,

$$f/s = \eta du/dz, \qquad (1)$$

η being the viscosity. This simple law holds for the classes of fluids in which we are here interested (water, water solutions, petroleum, etc.) but not for [1] fluids having the properties of either jelly or pitch, which do not ordinarily penetrate fine pores and within which intermolecular forces are not on the line between centres. Nor are we here concerned with turbulent flow. All quantities are of course in c.g.s. units.

The steps necessary to set up a flow formula applicable to any specific problem are as follows. First f/s is evaluated for any given surface where it is known. Then the general integral of (1) gives velocity u as a function of depth. Volumetric rate of flow (in c.c. per second) is the definite integral of u times the differential section in which it occurs. Mean velocity is the vol-

[1] P. G. NUTTING, this JOURNAL, May, 1921, pp. 679–685.

umetric rate of flow times the cross-section of the tube through which the flow occurs. This is the rate of advance and its time integral is the volumetric advance in a given time in cubic centimetres per second.

Interest here centres chiefly in pores of either tubular or lamellar (crevice) type. The active force is the resultant of those due to capillarity, hydrostatic head, atmospheric pressure, trapped gases, and the weight of the liquid itself. This resultant is put in the form of pressure P in dynes/cm.^{2} of cross-section, care being taken, in certain integrations, that weight is a function of height, and the pressure of a compressed gas a function of its compression.

In a tubular duct, the force acting to produce shear at any cylindrical surface at a distance r from the centre is $\pi r^2 P$. This acts over a surface whose area is $2\pi r x$, where x is the length already filled by fluid. Hence $f/s = rP/2x = \eta du/dr$. The integration of this gives velocity u as a function of radius r,

$$u = (R^2 - r^2) P/4x\eta, \tag{2}$$

the integration constant being determined from the condition that $u = 0$ for $r = R$, the radius of the wall. Total flow F (in c.c./second) is the definite integral of the flow in each cylindrical element, velocity times section, or $u.2\pi r dr$, the limits being $r = 0$ and $r = R$. This gives

$$F = \pi R^4 P/8x\eta. \tag{3}$$

The mean velocity $\bar{u}$ which determines the rate of advance through a pore is the total flow/total section, $F/\pi R^2$ or

$$\bar{u} = dx/dt = R^2 P/8x\eta. \tag{4}$$

This is half the maximum velocity (at the centre) given by (2) for $r = 0$.

Up to this stage it has not been necessary to distinguish between the different forms of forces tending to advance or retard the flow. But to integrate (4) and thus obtain $x(t)$, penetration as a function of time, it becomes necessary to specify the relation between P and x. Hydrostatic and atmospheric pressure and surface tension are independent of x, weight is proportional to x, while the back pressure due to compressed gas in a blind duct is proportional to the reciprocal of its length minus x.

In the special case of vertical ascent opposed by gravity and

viscosity, $P = 2\pi R\tau/\pi R^2$ (due to surface tension) $-\pi R^2 \times \rho g/\pi R^2$ (due to gravity). Hence $P/x = 2\tau/Rx - \rho g$. Substituting, the mean velocity (4) becomes

$$\bar{u} = dx/dt = a/x - b \qquad (5)$$

in which $a = R\tau/4\eta$ and $b = R^2\rho g/8\eta$. The maximum rise attained (call it H) is, from (5), $H = a/b = 2\tau/\rho gR$, being the value of x for $dx/dt = 0$. The integration of (4) subject to the condition $x = 0$ for $t = 0$ gives

$$-\log(1 - x/H) - x/H = bt/H. \qquad (6)$$

When the pores are very fine or are horizontal, the gravity term is negligible ($b = 0$) and (5) integrates into

$$x^2 = 2at = R\tau t/2\eta. \qquad (7)$$

Equation (6) also reduces directly to (7) for x/H small, whatever the value of b.

Equations essentially the same as (6) have been obtained by E. W. Washburn [2] and by C. E. Guye,[3] while (7) was obtained by Cude and Hewlett [4] and found to hold for substances like charcoal and water.

Lamellar voids in the form of minute cracks and fissures are not uncommon in rocks. Dye solutions and acids have been found in this laboratory to penetrate several inches even into granite and milky quartz of very fine texture. The formulæ applicable to this case are derived by taking the force per unit width acting to pull the fluid forward between parallel planes separated by a distance $2Z$, the variable distance z being measured outward from the centre. The force per unit area causing shear is $f/s = Pz/x = \eta du/dz$, hence $u = P(Z^2 - z^2)2\eta x$. Total flow $F = 2PZ^3/3\eta x$. Mean velocity $\bar{u} = F/2Z = PZ^2/3\eta x = dx/dt$. In this case the force per unit area (P) tending to advance the fluid is $2\tau/2Z$ due to surface tension, less that due to the weight of liquid $2Zx\rho g/2Z$. Hence $P/x = \tau/Zx - \rho g$ and corresponding to (5) for tubular ducts, we have for lamellar ducts

$$\bar{u} = dx/dt = A/x - B, \qquad (8)$$

in which $A = \tau Z/3\eta$, $B = \rho gZ/3\eta$ and $H = A/B = \tau/\rho gZ$, the

[2] E. W. WASHBURN, *Phys. Rev.*, **17**, 273–283, 1921.

[3] C. E. GUYE, *Arch. d. Sci.*, **7**, 63–68, 78–80, July-Aug., 1925.

[4] CUDE and HEWLETT, *J. Am. Chem. Soc.*, **42**, 391, 1920.

maximum height attained. The integration of (8) is precisely similar to that of (5) giving

$$-\log(1-x/H)-x/H=Bt/H. \qquad (9)$$

For very thin or horizontal crevices, $B=0$ and the solution of (8) is

$$x^2=2At=2\tau Zt/3\eta. \qquad (10)$$

Also for small values of x/H (early stages of advance) (9) reduces to $x^2=2At$ whatever the value of B.

The constants a and A may be interpreted as the velocities at unit depth due to surface tension opposed to viscosity, while b and B are decreases in velocity of rise due to the weight of liquid raised. The maximum height attained, H, may of course be obtained directly from the static equations $H=2\pi R\tau/\pi R^2\rho g=2\tau/\rho gR$, etc. Throughout the above discussion τ has for simplicity been used for the product of true surface tension and the cosine of the angle of contact. However, in all cases of good wetting (which is largely a matter of cleanliness of walls), that angle is nearly 90°.

By way of illustration, rough values of penetration and maximum height of rise are given in the following table for water, glycerine and a rather light mineral lubricating oil, each at about 20°C. = 68°F.

Flow Constants.

	Dens.	Visc.	S. Ten.	ρg	$\tau/2\eta=x^2/R$	$2\tau/3\eta=x^2/Zt$
Water	1.0	0.010	72	981	3600	4800
Min. Oil	0.8	1.0	30	786	15	20
Glycerine	1.26	10.0	64	1240	3.2	4.3

Maximum Heights Against Gravity.

	R = 0.1 mm.	R = 1 micron.	Z = 0.1 mm.	Z = 1 micron.
Water	14.7 cm.	1470 cm.	7.3 cm.	730 cm.
Min. Oil	7.6	760	3.8	380
Glycerine	10.3	1030	5.1	510

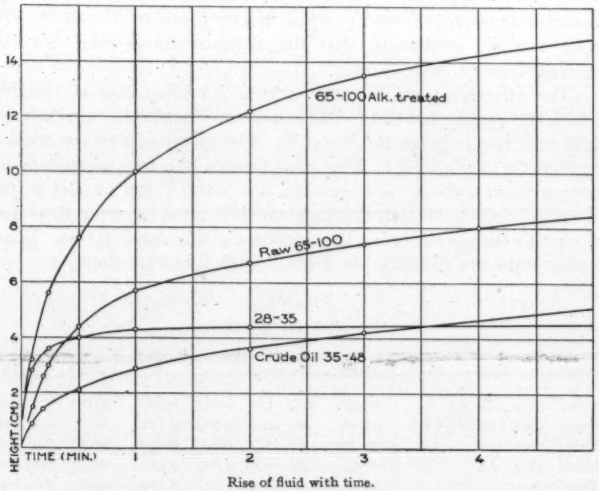
Time to Penetrate 10 Cm. Horizontally.

	R = 0.1 mm.	R = 1 micron.	Z = 0.1 mm.	Z = 1 micron.
Water	2.8 sec.	4.7 min.	2.1 sec.	3.5 min.
Min. Oil	11 min.	18 hours	8.2 min.	14 hours
Glycerine	52 min.	85 hours	38.8 min.	65 hours

Water would rise 30 feet in vertical tubular pores of 3.2 microns diameter. In flat rock crevices it would reach that maximum height if the crevices were 1.6 microns thick. A penetration

of 5 cm. in one hour into a rock with lamellar pores indicates an effective thickness of crevice of 1.5×10^{-6} cm., which is of the same order as the thickness of the layer of moisture (100 molecules deep) absorbed on quartz and many silicates exposed for some time to the atmosphere. The simple theory outlined above may not apply directly even to the case of water and silica and certainly

FIG. 1.



Rise of fluid with time.

would not apply to oil penetrating moist rocks. On the other hand, it is well known that when water is ascending in a column of sand or sandstone, the walls are moist far in advance of the filled capillaries.

In order to test formulæ (5), (6), (8) and (9) for natural pores, crooked and irregular in form and diameter, a series of measurements was made on sand in a half-inch vertical tube. Coarse cheesecloth over the bottom of the tube served to retain the sand. A wide dish of water or other fluid, into which the lower end of the tube just dipped, maintained a constant head of but one or two mm. The sand was sized with standard sieves

(openings in steps of root 2) and pre-treated in various ways. Readings of height of fluid were taken at intervals, repeated runs showing excellent agreement.

Mean effective diameter of pore and surface tension are obtained from the constants a, b, and H. Equations (6) and (9) between height and time are not readily solved for these constants but (5) and (8) indicate a linear relation between rate of rise dh/dt and reciprocal height $1/h$, $(dh/dt) = a(1/h) - b$. This linear relation was found to exist in every one of the thirty odd cases studied, indicating that the formulæ hold even for the extreme case of loose sand.

The effective pore diameter (from $b = R^2\rho g/8\eta$) is roughly a fifth the grain diameter. The maximum height H to which the fluid will rise is given by $H = a/b$. The effective surface tension is given by $(\tau = 4\eta a/R)$. This runs from a half to a seventh of its normal value (about 75 dynes/cm. for water) due in part to the increased length of path through which it must haul the fluid and in part to the condition of the surfaces of the sand grains. Some typical data are exhibited in Figs. 1 and 2 and in Table 1.

TABLE I.

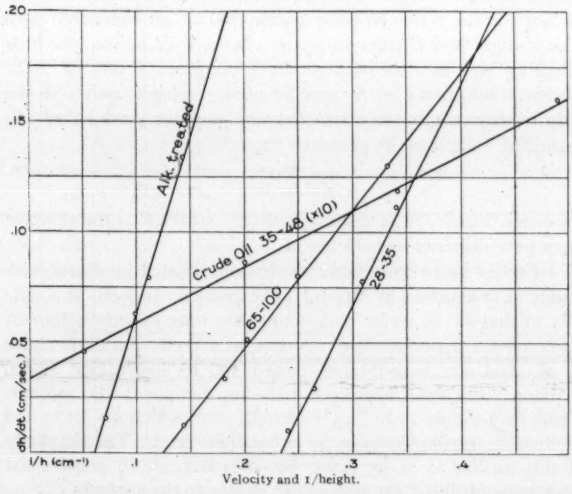
Rise of Fluid in Sand.

Fluid.	Sand.	Mesh.	Size (mm.).	a	b	R (cm.).	H	τ
Water	Sea (loose)	35–48	.417–.295	0.715	0.098	.0028	7.3	10.2
Water	Sea (packed 7%)	35–48	.417–.295	0.714	0.116	.0030	6.2	9.4
Water	Sea	65–100	.208–.147	0.628	0.079	.0027	7.9	9.4
Water	Sea	48–65	.295–.208	0.800	0.132	.0033	6.1	9.9
Water	Sea	35–48	.417–.295	1.01	0.179	.0038	5.6	10.5
Water	Sea	28–35	.589–.417	1.00	0.233	.0044	4.3	9.2
Water	Sea Dried	35–48	.417–.295	1.07	0.085	.0026	12.3	16.4
Water	Sea Acid ttd.	35–48	.417–.295	0.93	0.072	.0024	12.9	15.4
Water	Sea NaOH ttd.	35–48	.417–.295	0.48	0.050	.0020	9.6	9.5
Water	Sea Na_2CO_3 ttd.	35–48	.417–.295	1.43	0.075	.0027	19.3	23.3
Nujol	Sea Dried	35–48	.417–.295	0.065	0.0124	.0027	5.2	6.2
Crude Pet.	Sea Dried	35–48	.417–.295	0.103	0.0168	.0027	6.2	6.5
Water	Oil sand	65–100	.208–.147	0.134	0.0374	.0018	36.0	30.7

The effect of packing is but slight in sand of a narrow range of sizes. A moderate constant amount of packing was used throughout. In general the effective pore radius is difficult to determine

from the extreme range of sizes. The outstanding result is the very pronounced effect of pre-treatment of the sand grains. Merely driving off the film of adsorbed moisture (about 20 molecules deep, or 10^{-6} cm.) increases H by two or three times and the effect is greater with water than with oil as a fluid. Pre-treatment with acid has but a slight effect, as might be expected

FIG. 2.



Velocity and 1/height.

since the silica is itself acid. The effects produced by NaOH and by sodium carbonate treatments of sand grains are marked and very different from each other.

On the other hand, runs made with untreated sand and with water solutions of soda instead of pure water showed very little effect unless the solution was of high concentration approaching saturation. A crushed oil sand (Red River) showed very different capillary properties from sea sand of the same mesh, and did not show the great variations with drying or with chemical treatment shown by the sea sand. Data obtained with a heavy refined petroleum and with a high-grade crude (from Custer City,

Penna.) are added for comparison. In these cases R was assumed from previous determinations on the same sand and viscosity and surface tension computed from R and H. Throughout the work with water and water solutions as fluids, the viscosity of water (0.010 at 20°C.) was assumed.

The constants a, b, and H are experimental and independent of any assumptions. R was calculated on the assumption of an equivalent effective pore of that radius. The calculated effective surface tension τ involves the assumption of an equivalent pore both straight and circular in section, hence may be too low by a factor as high as 2 on both counts for a given R and H. The specific conductivity of a specific pore, in c.g.s. units, is the ratio of the velocity dh/dt to the net pressure gradient dP/dh producing it. Since in general (Eq. 4)

$$\frac{dx}{dt} = \frac{R^2}{8\eta}\frac{dP}{dx}$$

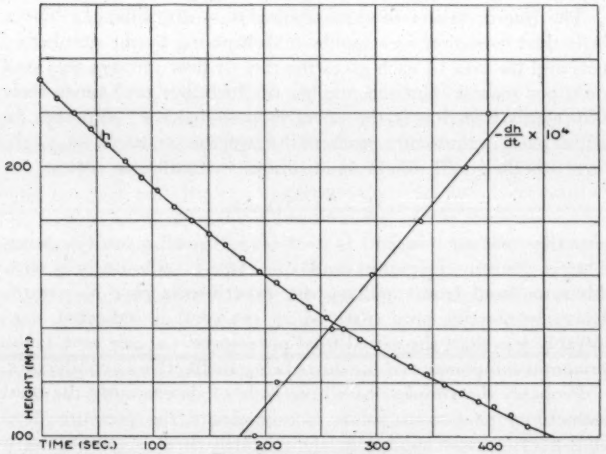
it follows that $R^2/8\eta$ is that conductivity, where R is the effective mean pore diameter as here found.

Effective mean pore diameters in consolidated sandstone may readily be determined by dipping a flat specimen (2.5 cm. is a suitable thickness) in water and noting the time of appearance of water on the upper surface. A section 2.5 cm. thick of a core of oil sand was heat treated, cooled and its lower face dipped in water. The water appeared on the top surface in 180 seconds. Hence by formula (7), $(2.5)^2 = 2a180$ from which $a = .0174$ and $R = 0.7\mu$, a reasonable value for a fine tight sand. The simplicity of this method is in its favor but it is difficult to prepare flat faces without filling the pores with débris at the surfaces.

In a unit cube of conducting porous material the effective (conducting) pore space is $n\pi R^2$, n being the number of effective pores per unit area perpendicular to the flow. But the total flow (in c.c./sec.) through the cube is $n\pi R^4/8\eta$ when the pressure gradient is unity. Hence the specific conductivity of a unit cube, namely the flow in c.c./sec. under unit pressure gradient, is $Q = R^2/8\eta$ times effective porosity. In other words, the specific conductivity (of a unit cube) is the conductivity of a single pore times the effective porosity. Our constant b as above determined is therefore a direct measure of conductivity, or permeability, as it is sometimes called.

The permeability toward water of building stones has been studied by D. W. Kessler [5] of the Bureau of Standards and of concrete by E. Anderson.[6] Both forced water through the specimen toward a dry side. Since the back capillary pressure ($P - 2\pi R\tau/\pi R^2 - 2\tau/R$) may amount to several atmospheres for the size of pores studied, a better arrangement would be to have water

FIG. 3.



Flow of water through oil sand.

on both sides and determine pressure differences. A mean effective pore radius of 1 micron would give with water a back pressure of 1.5 atmospheres, a radius of 0.1 micron, 15 atmospheres.

To further study specific conductivity in relation to size of pore, several inches of sand were placed in a vertical glass tube closed with coarse cheesecloth held by a rubber band at the bottom. Water was poured in at the top and the bottom kept just under the surface of a wide dish of water. Readings of the height of water column were taken every 15 seconds as it fell. Fig. 3 shows the curve obtained with a 65–100 mesh oil sand 10.3 cm. deep.

[5] D. W. KESSLER, Bur. Standards, Tech. Paper, No. 305.
[6] E. ANDERSON, *Jour. Ind. and Eng. Chem.*, Jan., 1926.

Such curves may be obtained with rather high precision. Their equation is of the simple flow type

$$-\frac{dh}{dt} = c\,(h - h_0), \tag{11}$$

the rate of fall of the column of fluid above the sand being a linear function of its height for any fluid whose flow is proportional to the pressure producing it. The values $c = .00210$ and $h_0 = 2.05$ cm. were obtained for the curve of Fig. 3.

The interpretation of these constants is not difficult. For a single duct, equation (4) applies. Multiplying by the number of ducts and the area of each gives the rate of flow through the sand in c.c. per second. But the number of ducts per cm.^{2} times their mean area of section is the effective pore space σ. Further, in (4), dP/dh, the pressure gradient through the sand is $(h-h_0)\,\rho g/l$, where l is the length of the sand column. Finally we obtain

$$-\frac{dh}{dt} = \frac{R^2\sigma}{8\eta}\cdot\frac{\rho g}{l}\,(h - h_0) \tag{12}$$

hence the constant c in (11) is $c = R^2\sigma\rho g/8\eta l$, all quantities being in c.g.s. units. For the sand of Fig. 3, $R^2\sigma = 1.77 \times 10^{-6}$. This same sand from capillary rise experiments gave $R = .0018$. Hence an effective pore space of 27 per cent. is indicated, considerably less than the actual total pore space (44 per cent.), the horizontal components of the ducts being ineffective as conductors.

Probably the simplest of all methods of determining the fluid conductivity of porous solids is to measure the pressure drop along a cylindrical conductor along which fluid is moving at a given known rate. However the experimental difficulties incident to determinations by this method are considerable and probably more accurate results be obtained by the method above described.

The rational definition of fluid permeability or conductivity is evidently the ratio of flow per unit area to the pressure gradient. In c.g.s. units, the specific conductivity is expressed in c.c./second /cm.^{2} per dyne/cm.^{2}/cm. This is the flow through a cube when the pressure difference between opposite faces is 1 dyne per cm.^{2} From (12) the conductivity of a porous solid for a fluid of viscosity η is $R^2\sigma/8\eta$, the factor ρg simply converts head into pressure units.

The wetting of surfaces of solids by fluids involves both chemical and physical causes. The theory of the advance of a wedge-

shaped film of fluid over a plane solid surface has yet to be developed. The advance of the thin edge undoubtedly involves chemical forces in the case of water and silica at least. Water rises through coarse sand by a succession of double steps; (1) a creep over the surface of each grain by the wedge action just mentioned followed by (2) a capillary leap to neighboring grains near points of contact. The rate of rise is limited chiefly by the rate at which the supply of fluid is kept up. Viewed under a microscope, the wetting of each grain appears to be almost instantaneous, the delay occurring mostly just before each leap to a fresh grain.

Very finely divided solids are almost impenetrable by water and some other fluids when not free to expand despite the powerful forward pull of capillarity. Fine clay, bentonite, shale, adobe and similar materials are familiar examples. The adsorption of water on silica and siliceous materials is well known to ceramists.[7] The writer has made many determinations of the thickness of the adsorbed layer on various materials. Specific surface in cm.^{2}/gram is determined either by direct measurement with a micrometer microscope or from the rate of fall through a water column. Specific moisture in grams/gram is determined by weighing and heating or desiccating. The ratio of these quantities gives the moisture/cm.^{2}.

Pure silica adsorbs at ordinary humidities 0.75 to 1.25×10^{-6} gm./cm.^{2} whether the particles be .01, 2 or 200 microns in mean diameter. Roughly half of this is removed by heating to 250° C. and as much more by heating to 800° C. The adsorbed layer on Al_2O_3 is about 3 times as deep as on silica, on Pt 11 times and on zinc dust (.07 mm. diameter) 14 times as much.

Evidently then a granular solid containing interspersed material having a grain diameter not exceeding 5×10^{-6} cm. (0.05 micron or 1/20 mm.) would carry sufficient adsorbed moisture to completely choke the pores. Near a free surface where the particles were free to separate from each other, the material would swell and become exceedingly slippery. If wet and then pressed or partly dried it would cake due to interlocking moisture films,

[7] BLEININGER and others, "Second Colloidal Symposium," 1925. C. S. Ross and E. V. SHANNON, *J. Am. Ceramic Soc.*, Feb., 1926. P. G. NUTTING, *Econ. Geology*, p. 326, May, 1926.

while in intermediate stages it is sticky or plastic. A size of grain of the order of .005 mm. is alone sufficient to account for such properties in any water adsorbing material.

The fall of a solid particle through a mass of fluid is an interesting special case of viscous flow. The active force is the weight of the falling particle, $\frac{4}{3}\pi r^3(\rho_2-\rho_1)g$ in dynes. This is proportional to the velocity v, the viscosity η and the perimeter $2\pi r$. Referring to our fundamental equation (1)

$$\frac{4}{3}\pi r^3(\rho_2-\rho_1)g = v.\eta.2\pi r.\text{ constant.}$$

The constant involves an integration of the velocity over the surface due to Stokes. Stokes' law

$$v = \frac{2}{9}(\rho_2-\rho_1)g\frac{r^2}{\eta}. \qquad (13)$$

gives a relation between velocity of fall, the densities of solid and fluid, viscosity of fluid and radius of particle.

For silica in water $v = 32700\ r^2$, hence a silica particle 0.11 mm. in diameter would fall at the constant rate of 1 cm. per second. A test with clean sea sand 65–100 mesh gave a close check with the formula. Metal particles such as zinc dust (200–300 mesh) and lead shot (1.38 mm.) showed a velocity but a quarter that computed, while Al_2O_3 particles (.006 mm. diameter, density 3.75) fell with six times the calculated velocity.

The layer of adsorbed water would retard the rate of fall of extremely fine particles if not readily replaced by fresh water, but the retardation would not be measurable except with particles less than 10^{-4} mm. in diameter. At all events it is unsafe to rely upon the Stokes formula for particles of this nature and size falling through water.

Molecular Weight of Egg Albumin.—The researches of THE SVEDBERG and J. B. NICHOLS, of the University of Upsala (*Jour. Am. Chem. Soc.*, 1926, **48**, 3081–3092), on the molecular weight of egg albumin in electrolyte-free solutions give a value of 34,500 ± 1000. Moderately pure egg albumin contains a small amount of another substance which has a molecular weight of approximately 170,000. These results were obtained by the centrifugal sedimentation equilibrium method for the determination of the molecular weight of proteins. J. S. H.

NOTES FROM THE RESEARCH LABORATORY, EASTMAN KODAK COMPANY.*

THE RECOVERY OF SILVER FROM EXHAUSTED FIXING BATHS.[1]

By J. I. Crabtree and J. F. Ross.

A PAPER dealing with methods of silver recovery, silver content of used fixing baths, possible financial returns, and the properties of the desilvered hypo. Experimental details on the following methods of silver recovery are given: (1) Precipitation with sodium sulphide; (2) precipitation by means of zinc in sheet, granulated, and powder form; (3) precipitation with sodium hydrosulphite; (4) electrolytic methods; (5) miscellaneous methods including precipitation with hydrogen sulphide, iron, aluminum, and magnesium.

The silver content of various exhausted baths was found to vary from 0.1 to 1 ounce (Troy) per gallon (0.7 to 7 grams per litre).

Cash returns on baths vary from 33⅓ to 50 per cent. of the value of the silver contained in the bath; an average bath containing approximately 0.5 cent worth of silver per average roll of Kodak film. Five gallons of exhausted hypo should be discarded weekly to make silver recovery profitable. For recovery of large volumes of fixing baths, the sulphide method is most efficient; for medium volumes, the zinc dust method is satisfactory, and for small volumes, the use of electrolytic unit offers a simple and economical procedure.

Experiments on the revival of the desilvered hypo baths, by the addition of a further quantity of hypo and acid hardener, demonstrated that satisfactory revival in many cases was possible, although it was concluded that it was more economical to prepare an entirely fresh bath.

A Further Study of the Inertia of the Electric Carrier in Copper. R. O. TOLMAN and L. M. MOTT-SMITH. (*Phys. Rev.*, Oct., 1926.)—If a metal contains free electrons, these should be to

* Communicated by the Director.

[1] Communication No. 280 from the Research Laboratories of the Eastman Kodak Company and published in *Amer. Annual Photography*, **41**: 159, 1926.

some degree independent in their motion of the state of motion of the metal surrounding them. In a coil of wire in rotation about its axis the free electrons rotate with the coil, but upon the sudden stoppage of the coil they keep on moving in the same direction as before. Thus within the coil there is a surge of negative electricity at the instant when the metal comes to rest. The existence of this momentary current was demonstrated and its strength was measured by Tolman and Stewart about ten years ago. The direction of the current produced was such as to show that the electrons had negative charges, and their mass came out 15 per cent. greater than it is in free space. In a later series of experiments a copper cylinder was oscillated about its axis with the result that an alternating current was set up, owing to the inertia of the electrons. This current was detected by its inducing a second alternating current in a coil of wire surrounding the cylinder. In the present experiment the same method is used. The oscillating copper cylinder was 9⅛ inches long with an outside diameter of four inches and inside diameter of three inches. The coil surrounding the cylinder consisted of 260,772 turns with a total length of 67 miles. This was connected through an amplifier to a tuned vibration galvanometer. Great care was exercised to eliminate the effect of the earth's magnetic field as well as all other possible sources of disturbance. The alternating electromotive force measured was found to be 19 per cent. less than that predicted by theory, while its phase lagged 10° behind that required by the same theory, which assumes that the electrons in a metal have the same mass as in free space. This discrepancy between experiment and theory remains to be explained, but there is no doubt that a current is caused by the inertia of the electrons within conductors.

G. F. S.

The Resistance of Gold, Zinc, Cadmium, Platinum, Nickel, Iron and Silver through Ranges of Temperature down to 1.3° Absolute. W. MEISSNER. (*Zeit. f. Phys.*, **38**, p. 647.)—The purpose of this research was to discover whether all metals share the property of superconductivity, that is, the practical disappearance of electrical resistance at very low temperatures, or do only certain metals, such as lead, attain this state. For the metals examined the minimum temperatures lay between 1° and 2° Abs. These were obtained by the evaporation of liquid helium. A single crystal of gold at 1.34° Abs. had .00029 of its resistance at 0° C. Single crystals of zinc at 1.67° Abs. still retained two or three thousandths of their resistance at 0° C. For 1.3° Abs. the values are as follows: Cadmium, 1.5 to 4.7×10^{-5} according to the direction in relation to the hexagonal axis; platinum, 1.65×10^{-3}; nickel, $5.02 \times ^{-3}$; iron, $21.56 \times ^{-3}$; silver, $6.79 \times ^{-3}$. While these fractions are small, they are far from indicating superconductivity. The employment of single crystals seems to have led to no new results of great value.

G. F. S.

NOTES FROM THE U. S. BUREAU OF CHEMISTRY.*

COMPOSITION OF THE ASH OF SPANISH MOSS.[1]

By Edgar T. Wherry and Ruth Buchanan.

[ABSTRACT.]

THE Spanish moss is an epiphyte, but not a parasite. The scales with which it is covered probably do not act to retard transpiration, but to hold water by capillarity while the plant is absorbing mineral constituents therefrom. Samples were collected from the seacoast in South Carolina and from far inland in Georgia, and the compositions of their ash determined, both with and without washing. A sample of Beard-lichen from Maine was also analyzed for comparison.

The analyses of washed and unwashed samples showed some differences, but these were not systematic and gave no indication that the washing removed adherent dust. The Spanish moss proved to be unusually high in soda, ferric oxide, sulphur, chlorine and silica. The chlorine was somewhat higher in the seacoast plant, and although the sodium was lower, this was connected with a much higher content of ferric oxide, diminishing all the other bases proportionately. Consideration of the composition of rain water shows that in general this plant does not take up constituents in the proportions present in the water, but exerts a marked selective action.

TOXICITY OF DIPYRIDYLS AND CERTAIN OTHER ORGANIC COMPOUNDS AS CONTACT INSECTICIDES.[2]

By C. H. Richardson (Entomology) and C. R. Smith (Chemistry).

[ABSTRACT.]

A CRUDE oil containing several isomeric dipyridyls and other substances was prepared from pyridine and sodium. The physical properties and chemical relationships of the dipyridyls were determined and their similarities to pyridine and nicotine studied.

In spraying experiments with six species of aphids, this crude

* Communicated by the Chief of the Bureau.

[1] Published in *Ecology*, **7**, July, 1926, pp. 303–306.

[2] Published in *Jour. Agri. Research*, **33**, Oct. 1, 1926, pp. 597–609.

dipyridyl oil was found to be highly toxic, but was surpassed in this respect by nicotine.

In submergence experiments, the crude oil was more toxic than nicotine to the larvæ of two species of *Coleoptera* and one species of *Lepidoptera*, and less toxic than nicotine to the adult of one species of *Coleoptera* and to silkworm larvæ.

Crude dipyridyl oil, in the present experiments, was not injurious to plants infested with aphids at concentrations sufficient to kill the aphids.

αα, ββ, βγ, and γγ dipyridyls, which occur in the crude dipyridyl oil used in these tests, were not so toxic to *Aphis rumicis* as the crude oil itself; γγ dipyridyl is much less toxic than the other three compounds.

Several preparations from the crude oil proved to be highly toxic to *Aphis rumicis* on nasturtium plants. Although unquestionably impure, they approached closely the toxicity of nicotine for this aphid. Work is being continued on these preparations.

The toxicities of sixteen other organic compounds tested during this investigation are given also (Table II). Several of these are related to the dipyridyls or to nicotine. As compared with dipyridyl oil, they showed no appreciable toxicity.

Crude dipyridyl oil was more toxic than nicotine to certain insects used in this investigation, and it is possible that it may also prove more effective for the practical control of some injurious insects.

A METHOD FOR THE STUDY OF THE FORMATION OF VOLATILE SULPHUR COMPOUNDS BY BACTERIA.[3]

By L. H. Almy and L. H. James.

[ABSTRACT.]

A METHOD for following the rate of hydrogen sulphide production by bacteria in broth cultures, recently devised in the Bureau of Chemistry, may be successfully applied under proper conditions to the study of aërobes, facultative anaërobes, and strict anaërobes.

The ratios of the amounts of hydrogen sulphide produced by *Proteus vulgaris* in twenty-four hours from five peptones on the market were found to be 1 : 7 : 15 : 19 : 24.

[3] Published in *Jour. Bacteriology*, 12, Nov., 1926, pp. 319–331.

A large proportion of the total hydrogen sulphide yielded by *Proteus vulgaris* and *S. aertrycke* from peptone in two days is produced in a comparatively short time in the early part of the incubation period.

Proteus vulgaris grew better and produced hydrogen sulphide faster from peptone under aërobic conditions than in the absence of oxygen.

Cystin gave practically the theoretical amount of hydrogen sulphide in peptone inoculated with *Proteus vulgaris*.

Three out of four authentic strains of *Proteus vulgaris* gave the same amount of hydrogen sulphide from peptone in twenty-four hours.

Tests for the formation of mercaptans by *Proteus vulgaris*, *S. aertrycke*, or *Esch. coli* from peptone during a two-day incubation were negative.

REMOVAL OF PLANT FOOD IN THINNING CORN.[4]

By Jehiel Davidson.

[ABSTRACT.]

CORN seedlings removed during two successive thinnings were analyzed to determine their content of nitrogen, potassium, and phosphorus. The pulled-out corn seedlings removed considerable quantities of nitrogen and potassium from the hills, but left behind small quantities of the phosphorus originally contained in the seed.

During the week between the first and second thinning about twice as much potassium and nitrogen was absorbed by the corn seedlings as during the period between planting and the first thinning.

Nitrates and ammonium salts were present in the young corn seedlings in appreciable quantities.

The application of sodium nitrate and ammonium sulphate increased the absorption of nitrogen, potassium, and phosphorus by the seedlings consistently during the period between planting and the time of the first thinning, but this effect became less pronounced a week later at the time of the second thinning.

It is important to thin promptly and avoid overplanting.

[4] Published in *Jour. Am. Soc. Agronomy*, 18, Nov., 1926, pp. 962–966.

THE PREPARATION OF 1, 4-DICHLORO-ANTHRAQUINONE FROM PHTHALIC ANHYDRIDE AND PARA-DICHLOROBENZENE.[5]

By Max Phillips.

[ABSTRACT.]

2', 5'-Dichloro-2-benzoylbenzoic acid has been prepared by condensing phthalic anhydride and *p*-dichlorobenzene, using anhydrous aluminum chloride as the condensing agent.

The 2', 5'-dichloro-2-benzoylbenzoic acid, when heated with sulphuric acid at 150°, was converted into 1, 4-dichloro-anthraquinone.

THE RÔLE OF THE PROTEOLYTIC ENZYMES IN THE DECOMPOSITION OF THE HERRING.[6]

By L. H. Almy.

[ABSTRACT.]

A BIOCHEMICAL investigation on the immature herring (used in sardine packing) to determine the cause of the decomposition of feedy fish, which makes them unacceptable for food purposes within a few hours, showed the following points.

The pepsin extracted with water from the stomach of the fish is more active at 37° than at lower temperatures and at hydrogen-ion concentrations between pH 2.5 and pH 2.85 than at higher or lower values. It is comparatively inactive above pH 4.0. Less pepsin is extractable from the stomach of feedy fish than from the stomach of non-feedy fish.

The trypsin extracted with water from the pyloric ceca is more active at blood heat than at lower temperatures and between pH 8.5 and 9.5 than at higher or lower values. It acts slowly, however, at pH 6.85. Decidedly more trypsin is extractable from the ceca of feedy fish than from the ceca of non-feedy fish.

In mixtures of ground flesh and digestive organs, enzymic digestion is rapid and is attributable mainly to the presence of the pyloric ceca. The stomach and intestines, as well as muscle autolysis, play only an insignificant part in the breaking down of the proteins.

[5] Published in *Jour. Am. Chem. Soc.*, **48**, Dec., 1926, pp. 3198–3199.

[6] Published in *Jour. Am. Chem. Soc.*, **48**, Dec., 1926, pp. 2136–2146.

The flesh of feedy fish is invaded by bacteria and by the trypsin of the pyloric ceca, but the visible evidence of decomposition—the softening of the abdominal wall—is due almost solely to the action of the trypsin, which is greater in amount or more active than that in the ceca of non-feedy fish, and which readily escapes from the delicate and highly congested tubules, quickly penetrating to the adjacent tissues of the ventral wall.

The Effect of Occluded Hydrogen on the Tensile Strength of Iron. L. B. Pfeil. (*Proc. Roy. Soc.*, A 760.)—For some time it has been believed that the rendering brittle of iron and steel by pickling in acid is due to the occlusion of hydrogen by the metal. Though this matter is of importance in tinning, galvanizing and wire drawing little is actually known of the effect of occluded hydrogen on tensile strength.

Measurements of tensile strength were made while the test pieces were in the acid. The specimen was surrounded by a glass tube holding the acid and was made the cathode, so that the hydrogen derived from electrolysis came to it. The material was mild steel from which all the carbon had been removed by long annealing. It contained small percentages of silicon, sulphur, manganese and phosphorus. Preliminary tests were made in the ordinary way without acid and showed an average tensile strength of 18.34 tons/sq. in. and elongation at fracture of 62.5 per cent. Then the effects of certain factors were investigated. Strength of acid made no difference. Change of current strength was without effect, provided rise of temperature was avoided. Test pieces were broken ¼, ½, 1, 2 and 18 hours after the current began to flow. A quarter-hour was too brief; a half-hour seemed adequate, but for safety an hour was the duration used. Test pieces of three diameters were broken and gave almost identical results, showing that the hydrogen had penetrated throughout in all cases. The time elapsing from the first application of the load until fracture seemed to make no difference. Temperature proved to be of much importance.

In the standard tests made with finely crystalline aggregates in 10 per cent. sulphuric acid at 25° C. after the current had been flowing for an hour, the tensile strength proved to be 16.7 tons/sq. in. or 9 per cent. less than without pickling, while the elongation was only one-sixth as much as before. The greatest difference, however, was in the manner of fracture. Without pickling the test piece formed a neck and then broke. With pickling the metal broke as if it were hard and brittle. The break took place suddenly before a neck developed, and passed between crystals and not through them. Upon raising the temperature a progressive increase of tensile strength and of elongation percentages was observed. The type of fracture also became different.

To study recovery from pickling, specimens were subject to the electrolytic hydrogen for an hour and then broken at intervals. After fifteen seconds the metal seems to have resumed its normal value of tensile strength.

Single crystals of iron hardly changed in tensile strength when pickled, though their elongation was reduced by 12½ per cent. The presence of hydrogen did, however, greatly change the appearance of the fracture. Cracks appeared running at right angles to the length of the test piece.

The author concludes that "occluded hydrogen has a remarkable weakening effect on the intercrystalline boundary. This applies not only to the boundaries between very large crystals, but also to the boundaries between the very minute crystals of which ordinary iron consists. In addition to its effect on the boundaries, hydrogen decreases the cohesion across the cubic cleavage planes, a pull of five tons per square inch applied at right angles to the cleavage plane being sufficient to cause separation." G. F. S.

Luminescence of Water and of Organic Substances Exposed to Gamma-rays. L. MALLET. (*Comptes Rendus*, July 26, 1926.)—Radium surrounded by two millimetres of platinum was placed in water. The metal let only 13 per cent. of the soft γ-rays pass and only 81 per cent. of the hard ones. The water then showed a white luminescence to the eye that had been kept in darkness for about fifteen minutes to increase its sensitiveness. When the layer of water surrounding the tube was thin the phenomenon was slight in degree, but its intensity increases with increase of the thickness of the water layer up to 8 or 10 cm. The additional water absorbed more of the γ-radiation. Thus more light was produced and, as this was but little absorbed by the water, a greater effect was produced upon the eye. The impartial photographic plate likewise registered the luminescent light from the liquid, care having been taken to allow for any direct effect of the γ-rays. The wave-length of the light coming from the water was roughly established as less than 3000 Å. U. from the fact that the interposition of glass between the plate and the water caused a much greater diminution of the photographic effect than was produced by using quartz and rock salt.

Transparent ice exposed to γ-rays was luminescent, too, but not to as great a degree as water at 20° C. Certain other transparent liquids displayed luminescence, such as alcohol, ether, chloroform and carbon disulphide. To a less extent the same effect was obtained with oils, fats and white wax. Albumin and blood-serum are likewise distinctly luminescent. These observations tend to complicate the understanding of the effect of exposing living tissue to X-rays, for now the action of the short wave-lengths from luminescence must be taken into account.

The investigator must have been fortunately placed, for he speaks of using 30 mg. of radium. G. F. S.

NOTES FROM THE U. S. BUREAU OF MINES.*

THE VAPOR PRESSURE OF ETHANE NEAR THE NORMAL BOILING-POINT.

By A. G. Loomis and J. E. Walters.

For the design of an efficient plant to extract helium from natural gas it is necessary to know the thermodynamic properties of the several components of the gas. This investigation by the Cryogenic Laboratory of the Bureau of Mines supplies the vapor pressure of ethane in the neighborhood of the normal boiling-point, and is one of a series of investigations now being undertaken on the thermodynamic properties of the pure components of natural gas, and of their binary mixtures. The pressures recorded cover the range from 0.0245 atmosphere to 2.1441 atmospheres; Doctor Porter,[1] of the Cryogenic Laboratory, has extended these measurements to the critical pressure.

The equation derived from the data representing P as a function of T is $\log_{10} P_{atm.} = -(780.24/T) + 4.2563 - 0.000103T - 9.3 \times 10^{-10}(T-238)^4$. The normal boiling-point is calculated to be $184.46_7°$ K. from this equation.

A deviation plot was prepared which compares the data of the several observers.

The latent heat of vaporization at the normal boiling-point of ethane is calculated to be 3642.4 calories per mole. Additional data will be found in a paper recently printed in the *Journal of American Chemical Society* (**48**, p. 2051, 1926).

HIGH VAPOR PRESSURES OF NITROGEN.

By Frank Porter and J. H. Perry.

The vapor pressures of nitrogen up to about one atmosphere have been measured by various investigators and accurately determined, but measurements of the higher pressures heretofore made are open to question for several reasons. The measurement of the vapor pressure of nitrogen over this range, therefore, was considered to be worth while.

The platinum-resistance thermometer and the cryostat used

* Communicated by the Director.

[1] *Jour. Amer. Chem. Soc.*, **48**, p. 2055, 1926.

have been described in previous reports. It was found convenient to use methane condensed from natural gas as a bath liquid for the lower temperatures. The pressures were measured with a deadweight gage of the type used by Keyes.

The vapor pressure of nitrogen has been determined in the range from 90.12° K. (3.631 atm.) to 121.47° K. (26.75 atm.). The results are represented fairly well by the equation $\log_{10}P = -302.34/T + 3.94127 - 0.00274T + 1.116 \times 10^{-6}(T - 100.5)^3$. A more complete description of the work is given in a recent paper published in the *Journal of American Chemical Society*.

ETHYLENE GLYCOL.

By C. A. Taylor and Wm. H. Rinkenbach.

ETHYLENE GLYCOL, $CH_2OH.CH_2OH$, the simplest of the polyhydroxy alcohols, has been of theoretical interest for many years; and during the past twenty years it was realized that many industrial possibilities were offered by the physical and chemical properties of the compound and its derivatives. However, the large-scale production of glycol has been economically feasible only during the past five years, and to-day it is a new and important industrial chemical because of its increasing use as a solvent, "antifreeze" component, and in the manufacture of glycol dinitrate. This last appears to become an important ingredient in dynamites for general and permissible uses.

Much miscellaneous, and in some cases contradictory, information concerning glycol is scattered through the literature. A program for the study of glycol dinitrate having been undertaken by the laboratory, it was considered advisable, in view of the growing importance of this new raw material, to collect, compare, and evaluate the information available concerning the physical properties of glycol itself. Details are given in a paper published in *Industrial and Engineering Chemistry*.

COKING OF OIL SHALES.

By W. L. Finley and A. D. Bauer.

THE Bureau of Mines, in coöperation with the State of Colorado, has investigated the tendency of oil shales to coke when heated and means for preventing the formation of dense hard coke. If the shale fuses during the retorting and forms a hard,

tough coke, removal of the spent shale becomes exceedingly difficult. This tendency to fuse is serious in only a few of the shales in this country, and can usually be easily corrected.

The fusing or coking property of shales does not bear any direct relationship to the yield or quality of the oil produced from the shale.

The coking shale does not coke when mixed with enough non-coking shale, or with enough spent shale, but the yield of oil is materially decreased by the latter method.

Saturated steam admitted to a retort that is heated externally prevents the shale from forming a coke as hard and dense as that ordinarily produced. Coking shale heated by steam that is superheated to 650° C. or higher forms a hard coke.

Oxidation at a temperature of 125 to 135° C. destroys the coking property of a coking shale. Oxidation also decreases the yield of oil.

The amount of material extractable from a shale by organic solvents is no indication of the coking tendencies of the shale. Further details will be found in Technical Paper 398 recently issued by the Bureau of Mines.

The Energy of X-rays. H. M. Terrill. (*Phys. Rev.*, Sept., 1926.)—This investigation has for its purpose the measurement of the total energy output of an X-ray tube in X-rays by having them absorbed and by determining the quantity of heat thus produced. Water-cooled Coolidge tubes were employed by which the double advantage was secured of reducing possible heat leakages into the measuring apparatus and of increasing the sensitiveness through the use of larger currents. The tubes were excited by constant potential direct current.

A pair of coils of lead wire were prepared of pancake type, 5 cm. in diameter and .28 cm. thick. Each had a resistance of 36 ohms. These two coils were connected as opposite arms in a bolometer. On one the X-radiation fell and the energy of this incident radiation was found by determining the energy imparted by that current which caused the same change in the resistance of the coil as was produced by the X-rays. Care was taken to protect the coils from outside radiation and from unequal temperature changes. In getting the current that caused the same temperature rise as the X-rays, it was not only the integral effect that was considered, but the rate at which the temperature rose. The current having been found that matched the X-rays in result, the energy of the radiation was calculated by the C^2R formula. The heat developed in five minutes was about

39×10^8 ergs. The radiated coil subtended .027 unit of solid angle or 1/466 of the entire sphere. In studying the efficiency of the tube at different voltages, the current was varied so as to maintain the output as given above approximately constant for all voltages. The X-radiation received by the measuring coil was 1/233 of the entire amount emitted through the hemisphere about the target. This divided by the input gives the radiating efficiency of the tube, no account being taken of the energy sent from the surface of the target into its own interior and there absorbed.

When the voltage was 30,000 the efficiency was .00025. This rises to .00192 when the voltage becomes 100,000. When efficiency is plotted against the squares of the voltages, the resulting curve consists of two straight lines joined at 69,000 volts. Very roughly it may be said that the efficiency is proportional to the square of the impressed voltage. It is known that the efficiency depends to some extent upon size and arrangement of the target and of the tube itself. The state of the surface of the target also is a factor. There therefore remains much room for further investigations of efficiency in the case of the X-ray tube. G. F. S.

Magnetic Properties of Iron Crystals. WALTHER GERLACH. (*Zeit. f. Phys.*, **39**, p. 327.)—Single crystals of iron possess magnetic properties that are different from those of ordinary ferromagnetic material. They have very small hysteresis, small remanence and coercive force. In addition their magnetization curve shows a sharp elbow at the point where it turns off toward saturation. When such single crystals or group of large crystals are bent and then straightened out again, their magnetic qualities suffer changes as well as their mechanical. "A wire 4 mm. thick composed of large crystals of iron can be bent into a ring without trouble. It cannot be bent back into its original form. It has become rigid. If force is applied to straighten out the ring, it breaks off smoothly. The surfaces of fracture are crystal surfaces that do not rust; at least they have not rusted up to the present, an interval of eight months."

The author relates very interesting sound effects obtained with single crystals, but a full description of the method employed is lacking. Stretching the crystal was without audible result. When the rod of iron, 6 cm. long and 3 mm. in diameter, composed of a single crystal, was supported at one end and a weight of a single gram attached to the other end, a noise was distinctly heard in the telephone. The same noise was noted when the weight was removed. From available data it was calculated that the average shift of position from atom to atom was of the order of 10^{-13} cm. Ordinary soft iron shows this effect quite clearly when bent, though steel does not. Stretching beyond the elastic limit produces sound. It thus seems that very small changes in the structure of matter may be detected by this method. G. F. S.

THE FRANKLIN INSTITUTE.

(Proceedings of the Annual Meeting, held Wednesday, January 19, 1927.)

THE annual meeting of The Franklin Institute was called to order at eight-sixteen P.M. by the President, Dr. Wm. C. L. Eglin.

The Secretary announced that the minutes of the preceding meeting had been published in full in the January number of the JOURNAL of the Institute and moved that they be approved as printed. This motion was unanimously adopted and the minutes were declared approved.

As this meeting was the occasion for the annual election, the Secretary presented the report of the Tellers—Dr. Henry Leffmann, Mr. W. N. Jennings, and Mr. T. S. McAllister, as follows:

Total number of votes cast.....415

No votes were recorded other than those cast for the officers whose names were printed upon the official ballot.

The President announced the election of the following:

President: (to serve 1 year), William C. L. Eglin.
Vice-president: (to serve 3 years), Walton Forstall.
Treasurer: (to serve 1 year), Benjamin Franklin.
Managers: (to serve 3 years), Charles E. Bonine.
Edward G. Budd.
Walton Clark.
Charles Day.
Clarence A. Hall.
George A. Hoadley.
James S. Rogers.
Haseltine Smith.
(to serve 1 year), Samuel T. Wagner.

A vote of thanks to the Tellers for their labors was then adopted unanimously.

The Secretary then reported the elections since the last monthly meeting: Number of new members—twenty-nine; resident members, six; non-resident, four; one contributing membership, taken out by one of the leading industrial concerns of Philadelphia for nineteen of its employees.

The Secretary made a report concerning the success of the experimental lectures for young people delivered during Christmas week by Prof. R. W. Wood. He stated that the attendance had been somewhat over a hundred per lecture and that the lectures had been greeted with great enthusiasm and were regarded as a thorough success. He reported that the Board of Managers of the Royal Institution of Great Britain had expressed an especial interest in The Franklin Institute and particularly in the newly established Christmas week lectures. As a token of friendship and good wishes, the Royal Institution had sent to The Franklin Institute an engraving of Faraday lecturing before the Royal Institution at a meeting attended by the Prince Consort, the Prince

of Wales and the Duke of Edinburgh; and also some coils of wire used by Faraday in his fundamental discovery of electric magneto induction. The engraving was on display and was open for inspection by the members at the end of the meeting.

The President presented an abstract of his annual report concerning the affairs of the Institute. The report will be published in full in the Year Book of the Institute.

The President then introduced as the speaker of the evening Mr. Thomas Midgeley, Jr., a distinguished research chemist of Dayton, Ohio, who read an interesting paper on "Anti-Knock Motor Fuel." Mr. Midgeley dealt with the theory and suggested explanations of the knock in automobiles, described much experimental work which had been done on this subject, and then dealt with the various types of anti-knock fuels and anti-knock substances.

The paper elicited a number of questions and a considerable amount of discussion.

The meeting was adjourned at ten-ten P.M., with a rising vote of thanks to Mr. Midgeley for his highly interesting paper.

HOWARD MCCLENAHAN,
Secretary.

COMMITTEE ON SCIENCE AND THE ARTS.

(Abstract of Proceedings of Stated Meeting held Wednesday, January 5, 1927.)

HALL OF THE COMMITTEE,
PHILADELPHIA, January 5, 1927.

MR. CLARENCE A. HALL *in the Chair.*

The following reports were presented for final action:

No. 2857: Method of Determining Stresses.

The purpose of this invention is to determine the stresses in structures resulting from the loads they are to carry. It is also designed to substitute a mechanical method for the mathematical analysis previously used.

The method employed is to cut from a sheet of celluloid, an accurately measured model of the proposed structure. This is supported in a horizontal position on a glass plate, small ball-bearings being placed between the model and the plate. Deformeter gauges are used to produce a known deflection at the points at which the stress is to be determined and a microscope with a micrometer eyepiece is used to measure the resulting deflection at the point of the assumed load.

If the change produced in the reading of the microscope is called d_2, the corresponding change in the reading of the gauge d_1, both being in the same units, the vertical reaction at the point of support at which the gauge is applied equals the ratio $\left(\frac{d_2}{d_1}\right)$ multiplied by the assumed load. The horizontal thrust and the moment can also be determined by similar measurements.

No. 2860: Power Drive for Typewriters.

The specific purpose of this invention is to provide means by which all the mechanisms on a typewriter, which are now manually operated, can be operated by power. In the operation of the type bar this result is secured by providing

a roller driven at a constant speed operated by motor installed in the frame of the instrument. A slight movement of the key releases a cam and brings it in contact with the revolving roller and this operates the type bar. This secures uniform typing irrespective of the force applied to the key. This uniformity of action is important in stencil cutting and in the making of carbon copies. The entire operation of the machine is from the keyboard.

In addition to the keys operating the type bars, suitable keys are also provided for the operation of the escapement, the platen shift, the carriage return, the back spacer, the tabular, or the automatic line spacer.

The following report was presented for first reading:

The Franklin Medal.

GEO. A. HOADLEY,
Secretary to Committee.

MEMBERSHIP NOTES.

ELECTIONS TO MEMBERSHIP.

(Stated Meeting, Board of Managers, January 12, 1927.)

RESIDENT.

MR. WILLIAM DEKRAFFT, Treasurer, Baldwin Locomotive Works, 500 North Broad Street, Philadelphia, Penna.

MR. ALFRED IDDLES, Engineer, Day and Zimmermann, 1600 Walnut Street. For mailing: 304 Conestoga Road, Wayne, Penna.

DR. JOHN M. MACFARLANE, Emeritus Professor of Botany, 4320 Osage Avenue, Philadelphia, Penna.

MR. STAUNTON B. PECK, Engineer and Manufacturer, in care of Link-Belt Company, Philadelphia, Penna. For mailing: Montgomery Avenue, Chestnut Hill, Philadelphia, Penna.

MR. WARREN P. VALENTINE, Mechanical Engineer, 713 Atlantic Building, Philadelphia, Penna. For mailing: Haddonfield, N. J.

DR. CLARENCE C. VOGT, Research Chemist, Armstrong Cork Company, Gloucester, N. J. For mailing: 408 Westmont Avenue, Haddonfield, N. J.

NON-RESIDENT.

DR. HOWARD M. ELSEY, Research Chemist, Westinghouse Electric and Manufacturing Company, East Pittsburgh, Penna. For mailing: 378 College Avenue, Oakmont, Penna.

MR. H. NAKAMOURA, Radio Engineer, Research Laboratory, The Tokyo Electric Company, Ltd., Kawasaki, Kanagawa-Ken, Japan.

MR. PHILIP SPORN, Electrical Engineer, American Gas and Electric Company, 30 Church Street, New York City, N. Y.

MR. CLIFFORD JOHN SUMMERS, Armature Winder, Nicolett, Minn. For mailing: U. S. S. New Mexico—Box 14, in care The Postmaster, San Francisco, Calif.

CONTRIBUTING.

LEEDS AND NORTHRUP COMPANY, 4901 Stenton Avenue, Philadelphia, Penna.
Representatives:
MR. MILTON B. BARBA, Sales Engineer.
MR. N. E. BONN, Electrical Engineer.

MR. NORMAN J. BRIGHTCLIFFE, Engineering Department.
DR. PAUL H. DIKE, Research Physicist.
MR. L. E. EMERICH, Salesman.
DR. WILLARD N. GREER, Research Chemist.
MR. JOHN W. HARSCH, Research Engineer.
MR. J. H. HAYNER, Chemical Engineer.
MR. JOSEPH C. HESS, JR., Assistant Superintendent.
MR. ATHERTON H. MEARS, Physicist.
MR. ROBERT D. MILNER, Salesman.
MR. DONALD E. MOAT, Sales Engineer.
MR. HARRY J. W. NETHERY, Research Department.
DR. HENRY C. PARKER, Research Department.
MR. SIDNEY B. RICKERSBERG, Mechanical Engineer.
MR. CRANDALL Z. ROSECRANS, Research Engineer.
MR. RAYMOND W. ROSS, Designer.
MR. FRANCIS H. WYETH, Engineering Sales.

TRANSFERS.

THE READING COMPANY, Philadelphia, Penna.
Representative:
MR. N. B. LEWIS.

CHANGES OF ADDRESS.

MR. RAYMOND BAILEY, Merion Cricket Club, Haverford, Penna.
MR. ARCHIBALD C. EGLIN, 55 Merbrook Lane, Merion, Penna.
MR. ROWLAND S. POTTER, in care of Defender Photo Supply Company, Rochester, N. Y.
MR. H. L. RANDALL, Riverside Metal Company, Riverside, N. J.
PROF. JOHN J. ROTHERMEL, 3126 Woodley Road, N. W., Washington, D. C.
MR. S. B. SKLAR, 536 Fremont Avenue, North, Minneapolis, Minn.
MR. C. F. SULZNER, San Sebastin Hotel, Coral Gables Station, Fla.
MR. HOLLINGSHEAD N. TAYLOR, Liberty Trust Building, N. E. corner Broad and Arch Streets, Philadelphia, Penna.
MR. EDWARD L. ZIESEL, 1732 Whitley Avenue, Hollywood, Calif.

LIBRARY NOTES.

RECENT ADDITIONS.

American Institute of Chemical Engineers.—Transactions, 1924. Volume 16, Parts 1–2. Two volumes. 1925.
Brassey's Naval and Shipping Annual, 1927.
Colloid Symposium Monograph. Volumes 2, 3, and 4. 1925–1926.
Dispensatory of the United States of America. Twenty-first edition. 1926.
DULL, RAYMOND W.—Mathematics for Engineers. 1926.
DWIGHT, HERBERT BRISTOL.—Constant-Voltage Transmission. 1915.
DWIGHT, HERBERT BRISTOL.—Transmission Line Formulas. Second edition, revised and enlarged. 1925.
Educational Aid Society.—College and Private School Directory of the United States. Volume 15. 1925–1926.

FLEMING, J. A.—Mercury-arc Rectifiers and Mercury-vapour Lamps. 1925.

HAWK, PHILIP B., and BERGEIM, OLAF.—Practical Physiological Chemistry. Ninth edition, revised and enlarged. 1926.

JUVET, G.—Mécanique Analytique et Théorie des Quanta. 1926.

KEASEY, MILES A., KLINE, G. ALFERD, and MCILHATTEN, D. ALLISON.—Engineering Mathematics with Tables. 1926.

March's Thesaurus Dictionary: A Treasure House of Words and Knowledge. 1925.

MAYER, EDGAR.—Clinical Application of Sunlight and Artificial Radiation. 1926.

PARCEL, JOHN IRA, and MANEY, GEORGE ALFRED.—An Elementary Treatise on Statically Indeterminate Stresses. 1926.

Royal Society of Edinburgh.—Transactions. Volume 54, Part 3. 1926.

SHELDON, SAMUEL, and HAUSMANN, ERICH.—Electric Traction and Transmission Engineering. Second edition, revised. 1920.

United States Patent Office.—Manual of Classification of Patents. 1923.

West Virginia Geological Survey.—Mercer, Monroe, and Summers Counties. Two volumes, text and plates. 1926.

BOOK REVIEWS.

MÉCANIQUE ANALYTIQUE ET THÉORIE DES QUANTA. Par G. Juvet, Professeur à l'Université de Neuchatel. vi–151 pages, 24.1 × 15.9 cm., paper. Paris, Librairie Scientifique, Albert Blanchard, 1926. Price, 20 francs.

The mathematical theories of the dynamics of the atom make use of the theorems of analytical mechanics and certain rules which relate to the theory of quanta. These theories are not entirely of a classical character and the author's object is to present the methods of analytical and celestial mechanics in a form adapted to facilitate their application to the quantification of the Bohr atom. The first part deals with these mathematical developments. The second part is devoted to the application of these methods to the theory of quanta.

The mathematical theorems and deductions are set forth in the highly generalized form that will especially appeal to the mathematical physicist.

THEORY OF VIBRATING SYSTEMS AND SOUND. By Irving B. Crandall, Ph.D., Member of the Technical Staff, Bell Telephone Laboratories, Inc. x–272 pages, 23 × 15 cm., cloth. New York, D. Van Nostrand Company, 1926. Price, $5 net.

There are to-day thousands of listeners to sound-producing devices where not many years ago only a handful ever heard anything else than the human voice, musical instruments or noises. Not every one attended musical performances frequently, and hearing operatic music over the house-telephone which it appears could be done in Paris thirty years ago was a rare novelty. Now, myriads of persons every day listen to the talking machine, the radio or the telephone. The obvious necessity of giving these devices, which have found application in every phase of human activity, the best attainable quality of performance has latterly given rise to an immense amount of intensive study to that end.

The present work, whose author is identified with the Bell Telephone Laboratories, is a brilliant example of this modern activity in the analytical study of vibrating systems and their application to sound. As stated by the author, "the treatment of the theory of sound is intended for the student of physics who has given a certain amount of attention to analytical mechanics and who desires a sufficient acquaintance with the theory of sound and its recent applications to bring it into balance with his studies in other branches of mechanical science."

As is well known, the theory of vibrating systems is capable of a high degree of mathematical development. The author has fully availed himself of this fact and of his own capacity as an analyst in presenting a rational and deductive treatise by modern mathematical methods. A sound knowledge of the general principles of physics on the part of the reader is premised, and many of the topics are of a character that demand a considerable amount of collateral reading, the many references to which are an excellent feature. There is also in an appendix an unusually full classified bibliography with brief notes on each entry.

The work is one that will tax the mathematical capacity of an undergraduate student and his general acquaintance with this branch of physics; it is rather in the post-graduate class and a valuable and timely addition to the literature of the subject. LUCIEN E. PICOLET.

ELEMENTARY MECHANISM, A TEXT-BOOK FOR STUDENTS OF MECHANICAL ENGINEERING. By A. T. Woods, M.M.E., and A. W. Stahl, M.E. Revised and rewritten by Philip K. Slaymaker, M.E., Professor of Machine Design, University of Nebraska. viii–250 pages, 23 × 15 cm., cloth. New York, D. Van Nostrand Company, 1926. Price, $3.

Among the subjects embraced in the practice of the machine designer's art, the study of mechanisms is second to no other one in importance. Except where great stresses are involved, the component elements of mechanisms, in so far as their dimensions to resist deformation are concerned, are frequently proportioned from manufacturing considerations rather than from the stresses which they must resist. The designer relies to a great extent on his sense of suitable proportion in that feature of the process of design, and many designers of machinery, of a past rather than of the present generation, have successfully followed their calling with little acquaintance with the principles of the mechanics of materials. No such freedom has the designer in determining the kinematic features of his creation; movements must take place according to prescribed magnitude and coördination. Many hours of needless labor can be saved in that part of the design process by a sound knowledge of the principles of mechanism over laborious and often imperfect tentative methods.

There is no lack of treatises and satisfactory text-books on the subject, the latter having generally been produced to meet special curricula. The original work upon which the present volume is based is one of these that amply proved its value by a demand for three editions and many reprints. In its present form much of the original has been rewritten and considerable material added. Particular attention may be directed to the discussion of the method of "instant centres" for determining velocities in linkages and the

chapters on gearing which are the present author's contribution. In the chapter on gearing, the involute system has been given the fullest attention rather than the cycloidal system as in the original work. The introduction of some modern applications with illustrations is an addition that should prove stimulating to the student.

A text-book is necessarily an abridgement and cannot possibly treat a subject exhaustively and this one has been judiciously compiled by a well-balanced selection of representative topics. The press-work is excellent and the work in its new garb is an attractive volume which should enjoy another long lease of life.

LUCIEN E. PICOLET.

LES FONDEMENTS DES MATHÉMATIQUES DE LA GÉOMÉTRIE D'EUCLIDE À LA RELATIVITÉ GÉNÉRALE ET À L'INTUITIONISME. Par F. Gonseth, Professeur à l'Université de Berne. Préface de M. Jacques Hadamard, Membre de l'Institut, Professeur au Collège de France et à l'École Polytechnique. xiv–243 pages, 25.1 × 16.5 cm., paper. Paris, Librairie Scientifique, Albert Blanchard, 1926. Price, 25 francs.

Fundamentals as defined in treatises on euclidean geometry and their analytic expression were formerly regarded proof against all exception, yet in modern times the universality of these fundamentals has been much under the scrutiny of celebrated analysts. Freed from the restrictions of commonplace applications, other conceptions of space have been evolved, and more latterly in their relation to time, by these leaders of mathematical progress. Mathematics is still taught under the commonly understood idea of space, doubtless from the fact that it meets the usual range of measurements applied in human affairs. Modern science, however, reaches out in an unrestricted field in which the old notions of space do not appear to suffice.

Professor Gonseth gives us here a rarely lucid account of just what the commonly defined fundamentals signify and a discussion of the newer concepts of space with their metaphysical arguments. In this the views of Dedekind, Poincaré, Weyl, Hilbert, and Einstein are freely drawn upon. Chapters on "time and relativity" and on "motion and general relativity" are much more within the capacity of the average mathematical reader than the usual explanations of these difficult concepts.

A work of this sort is a necessity to any one who would keep abreast with modern notions of mathematical fundamentals and this particular work presents that abstract subject in unusually attractive form.

LUCIEN E. PICOLET.

LES PHYSICIENS HOLLANDAIS ET LA MÉTHODE EXPÉRIMENTALE EN FRANCE AU XVIII^{e} SIÈCLE. Par Pierre Brunet, Professeur de l'Université. 153 pages, 25 × 16.5 cm., paper. Paris, Librairie Scientifique, Albert Blanchard, 1926. Price, 14 francs.

Some of the most notable contributions to physical science in recent times have been the gift of Dutch investigators, and those who interest themselves in the history of physics will learn that leadership in physical science of that country whose people have had such a wholesome and lasting influence in the development of this land, is not a present-day matter.

Professor Brunet precisely defines his aim in a lengthy introduction, which is briefly to depict the social and scholastic atmosphere which surrounds the historical facts of the development of the experimental method in Holland at the beginning of the eighteenth century. He describes at length how cartesian physics became supplanted by the newtonian philosophy and the experimental method practised in England. A second part deals with the influence of the Dutch school of physical science in France and to the extent with which students of French schools availed themselves of the teaching of celebrated Dutch physicists.

The volume is a noteworthy contribution in historical detail whose value is enhanced by a copious collection of references to original sources.

VAN NOSTRAND'S CHEMICAL ANNUAL. A hand-book of useful data for analytical, manufacturing, and investigating chemists, chemical engineers and students. Edited by John C. Olsen, A.M., Ph.D., D.Sc.; Assistant Editor, T. R. LeCompte, B.A., M.S., Ph.D. Sixth issue, 1926, thoroughly revised and enlarged. 882 pages, illustrations, folded diagrams, portrait, 12mo. New York. D. Van Nostrand Company, 1926. Price, $5.

The present edition of this well-known annual contains much new matter. New tables have been added on isotopes, hydrogen-ion concentrations and hydrogen values, specific gravity and solubilities, physical properties of lead and mercury, etc.

The text has been carefully reviewed and supplemented by the most recent data. A new bibliography of thirty-eight pages is also included. An excellent portrait of Dr. Svante Arrhenius adorns the volume.

NATIONAL ADVISORY COMMITTEE FOR AERONAUTICS. Report 241, Electrical Characteristics of Spark Generators for Automotive Ignition. By R. B. Brode, D. W. Randolph, and F. B. Silsbee. 32 pages, illustrations, quarto. Washington, Government Printing Office, 1926. Price, fifteen cents.

This paper reports the results of an extensive program of measurements on eleven ignition systems differing widely in type. The results serve primarily to give representative data on the electric and magnetic constants of such systems, and on the secondary voltage produced by them under various conditions of speed, timing, shunting resistance, etc. They also serve to confirm certain of the theoretical formulas which have been proposed to connect the performance of such systems with their electrical constants, and to indicate the extent to which certain simplified model circuits duplicate the performance of the actual apparatus.

Bibliography of Aeronautics 1923, published by the National Advisory Committee for Aeronautics. 144 pages, 8vo. Washington, Government Printing Office, 1926. Price, twenty-five cents.

The volume includes the literature published from January 1 to December 31, 1923, and continues the work of the Smithsonian Institution issued as volume 55 of the Smithsonian Miscellaneous Collections, which covered the material published prior to June 30, 1909, and the work of the National Advisory Committee for Aeronautics as published in the Bibliography of Aeronautics for the years 1909 to 1916, 1917 to 1919, 1920 to 1921 and 1922.

As in the Smithsonian volume and in the Bibliography of Aeronautics for the years 1909 to 1916, 1917 to 1919, 1920 to 1921, and 1922, citations of the publications of all nations have been included in the languages in which these publications originally appeared. The arrangement is in dictionary form with author and subject entry, and one alphabetical arrangement. Detail in the matter of subject reference has been omitted on account of the cost of presentation, but an attempt has been made to give sufficient cross-reference for research in special lines.

PUBLICATIONS RECEIVED.

Practical Colloid Chemistry, by Wolfgang Ostwald, Professor of the University of Leipzig, with the collaboration of Dr. P. Wolski and Dr. A. Kuhn. Translated by I. Newton Kugelmass, Sc.D., and Theodore K. Cleveland, Ph.D. 191 pages, illustrations, 12mo. New York, E. P. Dutton and Company, no date. Price, $2.25.

Investigations on the Theory of the Brownian Movement, by Albert Einstein, Ph.D. Edited with notes by R. Fürth, translated by A. D. Cowper. 124 pages, illustrations, 12mo. New York, E. P. Dutton and Company, no date. Price, $1.75.

The Calender Effect and the Shrinking Effect of Unvulcanized Rubber, by Dr. W. de Visser. Translated from the original Dutch by Edward S. Allsop. 152 pages, illustrations, 8vo. London, Crosby Lockwood and Son, 1926. Price, 15 shillings, net.

Van Nostrand's Chemical Annual. A hand-book of useful data for analytical, manufacturing and investigating chemists, chemical engineers, and students. Edited by John C. Olsen, Ph.D.; Assistant Editor, T. R. LeCompte, Ph.D. Sixth issue, 1926, thoroughly revised and enlarged. 882 pages, illustrations, folded plates, portraits, 12mo. New York, D. Van Nostrand Company, 1926. Price, $5.

Catalog of American Industry and Trade. (In the Russian language.) 1036 pages, illustrations, quarto. New York, Amtorg Trading Corporation, 1927.

Subject Index to Periodicals, 1922. Issued by The Library Association. K, Science and Technology. 271 pages, quarto. London, The Library Association, 1926. Price, £1, 1s.

Tables Annuelles de Constantes et Données Numériques d'Électricité, Magnétisme et Électrochemie rédigées, par Dr. A. Buffat, Dr. G. I. Higson et K. Gordon, M. Malapert. Préface de G. Semenza. Extrait du volume V, Années 1917–1922. 135 pages, quarto. Paris, Gauthier-Villars et Cie., 1926. Price, 56 francs, in paper; 77 francs bound.

U. S. Department of Agriculture: Department Bulletin No. 1449, Tumors of Domestic Animals, by Robert J. Formad, Associate Pathologist. 40 pages, 8vo. Bibliographical Contributions No. 12, Peat, a Contribution towards a Bibliography of the American Literature through 1925, compiled by Alice C. Atwood, Bibliographical Assistant. 95 pages, quarto. Washington, Government Printing Office, 1926.

National Advisory Committee for Aeronautics: Twelfth Annual Report, 1926. 69 pages, quarto. Technical Notes, No. 252, Resistance of a Fifteen-

centimetre Disk, by James M. Shoemaker. 3 pages, illustrations. No. 253, Wind Tunnel Standardization Disk Drag, by Montgomery Knight. 6 pages, illustrations, photograph. No. 254, Method of Correcting Wind Tunnel Data for Omitted Parts of Airplane Models, by R. H. Smith. 10 pages, photographs, quarto. Washington, Committee, 1926–1927.

An Attempt to Influence Artificially the Speed of Radio-active Change. B. WALTER. (*Zeit. f. Phys.*, 39, p. 337.)—In a radio-active series the change from one member to the next is accompanied by the emission of an α or β-particle from the nucleus of the atom. Up to the present time no means is known of changing in any way this spontaneous emission. From the layer of electrons that lies next to the nucleus it is, however, possible to release an electron by letting X-rays of appropriate hardness fall upon the atom. Walter conjectured that, when this layer has lost an electron, it may occasionally recoup its loss by getting an electron from the nucleus instead of by the customary process of gaining one from outer layers of the atom. If, indeed, an electron leaves the nucleus, then a change of the atom into the configuration of the adjacent member of the radio-active series has taken place.

Uranium X_1 was selected as a suitable radio-active substance for the experiment. It emits β-rays in changing to the next member of the series and its rate of transformation is so slow that X-rays may fall upon it for several days without prejudice to the results. The electrons ejected by Uranium X_1 have velocities lying between 1.44 and 1.77×10^{10} cm./sec. These speeds correspond to differences of potential ranging from 71 to 197 kilovolts. Accordingly the X-ray tube was operated at a pressure of 150,000 volts in the hope that electrons might be removed from the nucleus of the atoms. Specimens of the radio-active material were exposed to X-rays for nineteen hours but no change resulted that could not be explained by experimental errors. G. F. S.

Depression of the Barometer to the Leeward of a High Obstacle. MESSRS. CHARCOT and IDRAC. (*Comptes Rendus*, Nov. 3, 1926.)—Jan Mayen Island is made up in great part of a volcano, 2300 metres in height, whose sides fall abruptly to the sea. The vessel, *Pourquoi-Pas*, engaged last summer in oceanographic work near this island, was twice obliged to seek shelter in its lee from violent wind. On one of the occasions the barometers on board showed a depression of 1.8 mm. when the calm area behind the island was reached. Off the island the wind velocity was 13 metres per second. At the other time the depression was 2.5 mm., the outside wind velocity amounting to 18 or 20 metres per second. This effect is ascribed to a strong ascending current of air in the lee of the volcano. The wind is split by the mountain. The partial currents flowing around the two sides meet behind it and make their escape upward. G. F. S.

New Test for Cyanic Acid.—WILLIAM ROBERT FEARON, of Trinity College, Dublin, Ireland (*Jour. Biol. Chem.*, 1926, 70, 785–792), has devised the following test for cyanic acid and its salts. The reagent is prepared by addition of two to five drops of a 6 per cent. solution of benzidine in alcohol and several drops of a 6 per cent. solution of cupric acetate to 5 c.c. of water, and mixing. The cyanate solution, which must be either neutral or faintly acid, is added to the reagent. A purple color develops, and rapidly changes into a sepia precipitate, which soon deposits. This test will reveal the presence of 0.1 milligram, and even less, of potassium cyanate. Alkalies inhibit formation of the colored compound; certain compounds interfere with the test, acids decompose the colored compound and hydrolyze the cyanate, sulphates precipitate the benzidine, and cyanides, thiocyanates, thiosulphates, iodides, and bromides react with the reagent to form dense colored precipitates. The precipitate yielded by cyanates contains one copper atom, two cyanate radicals, and one benzidine molecule; its formula is: $Cu(OCN)_2.NH_2.C_6H_4.C_6H_4.NH_2$, both amino groups being in the para position. The reaction may be used for the quantitative determination of cyanates, collecting the precipitate on a filter, washing with water and alcohol, and drying.

This test cannot be applied directly to the solution obtained on digestion of urea with urease, since urease interferes with the reaction. However, if the digested solution be treated with an excess of normal silver nitrate solution, a precipitate is produced. If this precipitate be mixed with the cyanate reagent, and the mixture be carefully acidified with tenth normal hydrochloric acid, the characteristic cyanate reaction is obtained, showing that silver cyanate was present in the precipitate, and that a cyanate was one of the products formed during the enzymic hydrolysis of urea. J. S. H.

Citric Acid Content of Milk. F. F. SHERWOOD and B. W. HAMMER (*Agric. Exp. Station Iowa State College of Agric. and Mechanic Arts Research Bull. No. 90*, 19–39, 1926) have determined the citric acid content of 335 samples of milk obtained from 20 individual cows, including five Jerseys, three Guernseys, seven Ayrshires, and five Holsteins. The cows were on pasture during the summer and received a liberal supply of silage in the winter. The citric acid content of the milk ranged between 0.07 and 0.33 per cent., with an average of 0.18 per cent.; it apparently was not influenced by the season, the stage of lactation, the time of day of milking, or the breed. In these 335 samples of milk, the acidity, calculated as lactic acid, ranged between 0.10 and 0.25 per cent. with an average of 0.17 per cent., the ash between 0.38 and 1.10 per cent. with an average of 0.70 per cent., the fat between 1.60 and 9.20 per cent. with an average of 4.58 per cent., the total solids between 8.82 and 20.15 per cent. with an average of 13.52 per cent. When the total solids were calculated as the sum of one-fourth the lactometer reading plus

1.2 times the fat, the calculated value tended to be higher, rather than lower, than the value obtained by analysis.

The citric acid content of 27 samples of cream obtained from a separator ranged between 0.09 and 0.19 per cent. with an average of 0.13 per cent., while the citric acid content of 26 samples of mixed farm cream ranged between 0.10 and 0.20 per cent. with an average of 0.15 per cent. No evidence was obtained of a seasonal variation in the citric acid content of cream. J. S. H.

New Indicators.—BARNETT COHEN, of the Hygienic Laboratory, U. S. Public Health Service (*Public Health Reports*, 1926, **41**, 3051–3074), describes six new compounds of the sulphonephthalein series which are of value as indicators in volumetric analysis and as reagents for the colorimetric determination of hydrogen-ion concentration. The new compounds have the following scientific names, proposed common names, useful pH range, and color change in passing from acid to alkaline: Tetrabrommetacresolsulphonephthalein (brom cresol green), 3.8 to 5.4, yellow to blue; Tetrachlormetacresolsulphonephthalein (chlor cresol green), 4.0 to 5.6, yellow to blue; Dibromphenolsulphonephthalein (brom phenol red), 5.2 to 6.8, yellow to red; Dichlorphenolsulphonephthalein (chlor phenol red), 4.8 to 6.4, yellow to red; Dibromdichlorphenolsulphonephthalein (brom-chlor phenol blue), 3.0 to 4.6, yellow to blue; Metacresolsulphonephthalein (metacresol purple) with a dual pH range and color change, *i.e.*, 1.2 to 2.8, red to yellow, and 7.4 to 9.0, yellow to purple. J. S. H.

Faught Test for Acetone.—In this test, the unknown solution is mixed with an aqueous solution of sodium nitroprusside. Then several drops of an aqueous solution of ethylene diamine hydrate are added as an upper layer. If acetone be present, a pink or red zone forms at the line of contact. The solution of sodium nitroprusside must be freshly prepared. HARRY J. SCHAEFFER, of the Philadelphia College of Pharmacy and Science (*Am. Jour. Pharmacy*, 1926, **98**, 643–645), has studied the relative sensitivity of the various tests for acetone. He finds that the Faught test is the most efficient and delicate, and is of extreme value when small quantities of acetone are to be detected. He reports the delicacy of the various tests for acetone as follows: Dibenzalacetone 1 : 500, Lieben 1 : 1000, Kolthoff 1 : 2500, Legal 1 : 10,000, Faught 1 : 100,000. J. S. H.

Professional Engineers. More Than 3000 in United States Civil Service.—The United States Civil Service Commission has just issued an interesting pamphlet which describes the work of engineers in the Federal executive civil service. There are more than 3000 civilian professional engineers in the Government's employ.

Federal engineering operations are carried on in practically every part of the United States, and extend to Alaska, Guam, Hawaii,

Panama, the Philippine Islands, Porto Rico, and Samoa. The activities of a Federal engineer may take him on a boat trip down the Grand Canyon of the Colorado, or to the potential oil fields of northernmost Alaska, where he must travel by dog train. Again, he may be called to the wooded Adirondacks, to a western Indian reservation, or to the plains of Texas. He may be assigned to a tour of duty in Panama where a narrow strip of civilization is bordered by primitive jungles, in tropical Hawaii, or in the Philippine Islands still farther to the westward. The opportunity is no less good for the engineer who prefers specialization in some particular branch of his profession and location at one place with perhaps incidental trips from time to time.

Nearly 700 civilian engineers are employed in the various divisions of the War Department. The Department of the Interior engages the services of 600 engineers, the Department of Commerce 600, the Department of Agriculture 450, the Navy Department 350 civilian engineers, the Treasury Department 250, and the Interstate Commission 200. A considerable number are included in the forces of the Veterans' Bureau, the National Advisory Committee for Aeronautics, and various other bureaus.

The activities of the Government's engineering force embrace practically every branch of endeavor to which engineering is applied. Road building, construction of various types ranging from lighthouses to large public buildings, conservation of national resources, research and testing covering an extensive field, cadastral surveys and topographic work, irrigation projects, valuation of railroads and natural resources, aeronautical studies, sanitation, improvement of waterways, building of ships, and the design and development of munitions represent only a few of the Government's operations which require the services of engineers.

Many branches of the Federal service offer engineers unique training and experience, inasmuch as the research studies carried on are not duplicated in private industry. Examples of these are the dust-explosion investigations of the Bureau of Chemistry, the work of the Fixed-nitrogen Research Laboratory, the wood-research activities of the Forest Products Laboratory, and the helium studies of the Bureau of Mines. Unusual projects are also undertaken. In research and development in new branches of engineering endeavor, the Government often leads the way. Excellent experience may be gained in the fields of radio and aeronautics, and also training for work in many commercial industries such as, for instance, those which manufacture celluloid and rayon.

Young engineers entering the Government service are afforded, in Washington and in many of the district headquarters of the various Federal establishments, an opportunity to pursue educational courses at hours which do not conflict with their working hours. A number of Government field stations and laboratories are maintained in coöperation with universities and technical schools where special

courses may be arranged. Several Government establishments also give valuable courses in technical and professional lines which are arranged at hours convenient to employees.

The contacts which the Government service affords young engineers are exceptionally good. In and out of their places of duty, they come in contact with men of national, and even international, reputation whose collective interests cover the entire field of engineering. As a result of contact with prominent manufacturers, many engineers in the Federal service have found a Government position the stepping stone to a more highly remunerative one in private industry.

Examinations for positions of junior engineers are held ordinarily two or three times a year, in accordance with the needs of the service. Examinations for the higher grades are held from time to time as vacancies occur.

Persons who desire to be notified of the announcement of an examination for engineers of any grade, or in any specialty, may place their names on file for that purpose with the United States Civil Service Commission, Washington, D. C. The Commission will be glad to send a copy of pamphlet form 2599, "Opportunities for Engineers in the United States Civil Service," to any one who is interested.

THE FRANKLIN INSTITUTE

OFFICERS FOR 1927

President	WM. C. L. EGLIN
Vice-presidents	HENRY HOWSON C. C. TUTWILER WALTON FORSTALL
Secretary	HOWARD MCCLENAHAN
Assistant Secretary and Librarian	ALFRED RIGLING
Treasurer	BENJAMIN FRANKLIN
Controller	WILLIAM P. JACKSON, JR.

Board of Managers

JAMES BARNES
GEORGE H. BENZON, JR.
CHARLES E. BONINE
EDWARD G. BUDD
FRANCIS T. CHAMBERS
G. H. CLAMER
THEOBALD P. CLARK
WALTON CLARK
CHARLES DAY
ARTHUR W. GOODSPEED
CLARENCE A. HALL
ALFRED C. HARRISON
NATHAN HAYWARD
GEORGE A. HOADLEY
ROBERT W. LESLEY
MARSHALL S. MORGAN
CHARLES PENROSE
JAMES S. ROGERS
GEORGE D. ROSENGARTEN
E. H. SANBORN
HASELTINE SMITH
SAMUEL T. WAGNER
J. T. WALLIS
WILLIAM C. WETHERILL

PRESS OF
J. B. LIPPINCOTT COMPANY
PHILADELPHIA